VOLUMETRIC ANALYSIS

Volume II

VOLUMETRIC ANALYSIS

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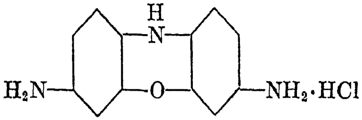
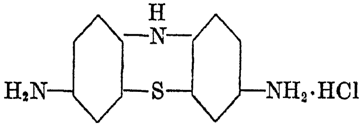
Errata

VOLUMETRIC ANALYSIS, Volume I

Page 113. The reduced form of diaminophenoxazine should be:



Page 114. The reduced form of diaminophenothiazine should be:



Page 141, line 7. Replace "Volume II" by "Volume III"
Page 231, line 6. Delete "it"
Page 253, line 18. Replace "Volume II" by "Volume III"
Page 292, Table VII, last column, fifth line up (for benzene). Change "1.5" to "1.1"

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This book is dedicated
to the memory of the late
PROFESSOR N. SCHOORL

"The theory guides,
The experiment decides."

PREFACE

The contents of this book are based upon a German monograph, *Die Praxis der Massanalyse*, published in 1928 by the senior author with the assistance of Dr. H. Menzel of Dresden, and revised in 1931. The first edition was translated into English by Dr. N. H. Furman in 1929. Because of the many contributions that have since been made in the field of volumetric analysis, an up-to-date revision of the book has been urgently needed. This volume is offered as a comprehensive, modern text presenting critically selected methods for the volumetric determination of various inorganic and organic substances. It would be impossible, and probably undesirable, to give a detailed discussion of all the methods that have been proposed. In order to treat even the more useful ones with some degree of thoroughness it has been found advisable to prepare two volumes instead of the one which was originally planned. Oxidation-reduction methods have therefore been reserved for Volume III; the present book includes, with considerable revision and numerous additions, all other material given in Volume II of the previous editions.

No effort has been made to cover exhaustively all applications of volumetric methods to specialized subjects in technical analysis. Instead there is given a somewhat arbitrary selection of useful and reliable procedures for certain purposes. For example, the reader will find directions for the determination of calcium, magnesium, carbon dioxide, bicarbonate, sulfate, chloride, and fluoride in water, and of many substances in industrial, pharmaceutical, and agricultural products. The arrangement of the methods is determined by the type of reaction involved in the titration rather than by the field in which it may be applied. In this way the authors seek to emphasize the fundamental principles upon which each method is based. Applications are given in notes following the procedures.

The plan of this volume follows that of its predecessors. Volumetric glassware, calibrations, and standard substances are considered in the first two chapters, and acid-base titrations in the third and fourth. The next three chapters (V–VII) deal also with acid-base reaction methods, but more particularly with those involving displacement, hydrolytic precipitation and complex formation. Chapter VIII, which previously covered all precipitation reactions, in this edition is devoted entirely to argentometric methods. Other precipitation methods are discussed in Chapter IX, which includes much new material. Procedures dependent on the formation of slightly dissociated compounds (other than those involving the titration of hydrogen ions) are described in the tenth chapter.

Since an understanding of theoretical principles is essential in evaluating and improving analytical methods, the theory underlying the more important procedures is generally outlined with reference to Volume I. In many cases the limitations of methods have been investigated by the authors and their co-workers, with the aim of selecting only the more reliable procedures and of providing knowledge concerning precision and accuracy. This material is usually given in notes following the procedures, together with mention of interfering substances and ways of removing them or counteracting their effects. The reader is strongly urged to study the notes as thoroughly as he does the manipulative details.

Because of obstacles which understandably but regrettably hindered a free flow of information during the war years, the book does not include a complete discussion of methods published abroad since 1940. The authors will welcome suggestions for the incorporation of new methods and constructive criticism concerning errors or omissions.

It is a pleasure to acknowledge the help which has been received from several friends and colleagues. Dr. Marian S. Bushey has been of much assistance with the material in Chapters I and II, and Dr. A. S. O'Brien with that in Chapters VIII and IX. Mr. A. W. Beshgetoor has again read most of the manuscript and given suggestions based upon his long industrial experience. Secretarial help has been furnished by Mrs. Bion McPeak, whose careful workmanship and chemical training have eliminated many potential sources of typographical errors. Various workers have contributed information from their practical experience; their cooperation is acknowledged in the text.

I. M. Kolthoff
V. A. Stenger

Minneapolis, Minnesota
Midland, Michigan
February, 1947

PREFACE TO THE FIRST GERMAN EDITION

During the writing of the "Theoretical Principles of Volumetric Analysis" (Volume I of this book) the author did not at first have the intention of following it with a practical treatise because of the idea that the present demands were satisfied by the excellent work of Prof. H. Beckurts, in collaboration with Dr. O. Lüning, entitled "The Methods of Volumetric Analysis"—a revised edition of Dr. F. Mohr's "Textbook of Chemical-Analytical Titration Methods." For various reasons, however, the author decided to write this "Practice of Volumetric Analysis" in connection with the "Theoretical Principles." Beckurts' book originated in the year 1913; since that time applied titration methods have experienced an immense development, so that perhaps many chemists feel the need of an up-to-date, critical, comprehensive work on volumetric analysis, which is the most interesting and versatile branch, on the whole, of analytical chemistry.

This book is by no means intended to include all titration methods that have ever been published. We have rather limited ourselves to those that have an actual practical significance and that have proved to be reliable and free from objection. In the majority of cases the author considered it mandatory that he himself should test the methods critically and give his judgment. Therefore the book has a strongly personal touch; the author is fully conscious of the great responsibility that he has thus taken upon himself. But this personal judgment here and there is exactly the thing which will perhaps be of value and interest to many readers. Many of the methods discussed are still far from complete. Errors through overestimating the value of one method or condemning another unduly are unavoidable. The author welcomes constructive criticism from his professional colleagues, calling his attention to omissions and errors.

Especial emphasis has been placed upon the numerical accuracy of the various titration processes. It was therefore necessary to precede the methods *by general considerations regarding the accuracy of the customary measuring flasks and apparatus, and concerning the limits of accuracy in standardizing the solutions* (Chapter I). According to the precedent established by S. P. L. Sörensen, the distinction between the fundamental *primary standards* and *secondary standards* that are practically useful has been specially emphasized (Chapter II).

Special consideration is given to the *purification* and *tests of purity* of the standard substances in the different sections of the book. The accuracy of all volumetric methods depends primarily upon the accuracy with which the solutions are standardized—and this in turn necessarily depends upon the purity of the primary standards. These important matters have not been hitherto sufficiently appreciated and in most works of reference on volumetric analysis they are only touched upon briefly. In many cases there are not available exhaustive processes for testing the primary standard; it is exactly at this point that there is still much systematic work to be done, with data, as far as possible, upon the limits of sensitivity of the reactions that are used in the tests.

We have here followed the customary division and classification of the underlying chemical reactions that we have already followed in the theoretical treatment (Volume I). Our arrangement is somewhat arbitrary for procedures that touch upon various individual types of reactions (for example, precipitations in connection with neutralization processes); ordinarily the reaction that is connected with the final measurement decides the classification—but for the sake of a comprehensive view of a whole field we have here and there departed from this principle of arrangement. The extensive subject index will make the search for the methods easier in doubtful cases of classification.

The treatise of Beckurts that we have cited has been of inestimable service in writing this book. The historical development of the methods has been so clearly and completely presented there that the author has foregone any exhaustive historical observations and has for the most part rested content with a brief synopsis. This "Volumetric Analysis" by no means should or can replace Beckurts' important text, but might find a friendly reception as a supplement and extension of that work.

I. M. Kolthoff

Minneapolis, Minnesota
January, 1928

From the translation by N. Howell Furman,
Princeton University, 1928

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A. APPARATUS AND GENERAL PRINCIPLES

CHAPTER I

CALIBRATION AND USE OF VOLUMETRIC APPARATUS

1. Introductory Considerations.—During the development of analytical chemistry numerous kinds of measuring vessels and apparatus have been proposed. Only those which have proved to be generally acceptable will be discussed here. For making volumetric measurements glass equipment is employed almost exclusively, though quartz ware or plastics might conceivably be used for special purposes.

Since practically all liquids except mercury will wet glass surfaces, measuring vessels are especially calibrated according to whether they are "to contain" or "to deliver." In the case of apparatus made "to contain," the content when filled to the mark represents exactly the desired volume of liquid. The liquid required to wet the walls is included as part of this volume. A vessel which is calibrated "to deliver" yields, on emptying, the predetermined quantity of liquid. Such a vessel when filled to the mark must contain in addition to the delivery volume as much more liquid as corresponds to the wetting of the walls and delayed drainage. Since these factors depend upon the nature of the liquid and the manner of calibration, they will be considered more thoroughly later.

The kind of calibration, whether to contain or to deliver, is usually marked on the vessel. Equipment calibrated both to contain and to deliver is not to be recommended because errors can easily occur.

In general, volumetric glassware should fulfill the following specifications:

(*a*) The vessels shall be reasonably resistant to chemical and thermal action and shall be made of glass (or quartz) as free as possible from hysteresis effects.

(*b*) The cross section of the vessel should as a rule be circular and may be oval only in exceptional cases. The transition from narrower to broader parts must take place regularly and gradually.

(*c*) Stopcocks, stoppers and thermometers, insofar as the latter serve as stoppers, must fit in liquid-tight fashion.

(*d*) Discharge and overflow tips must be straight, and their orifices should be smooth and may be drawn out somewhat; for Gay-Lussac burettes they must be ground off diagonally at the bottom.

(*e*) The marks shall be straight, continuous, sharp, and symmetrical, without notches, and may be enameled or colored. They must lie in a plane normal to the axis of the vessel and shall not be located within 0.5 cm. of the beginning of a bulge or constriction. The marks must extend at least half way around vessels of circular cross section. Shorter marks are permissible only if an unequivocal reading can be assured, or when the cross section is oval. With vessels of oval cross section the longest marks must extend nearly across the front surface and the shortest over at least half of the strongly curved surface. The marks must be clearly numbered, the location and form of the figures being such that no confusion is possible.

(*f*) The spacing of the divisions shall be uniform and without evident error, at intervals of at least a millimeter.

2. Cleanness and Cleaning of Glass.—According to various authors the concept of a "clean glass wall" needs an exact definition, but Schloesser[1] regards this as unnecessary. If water will drain off freely, wetting the surface uniformly without leaving streaks or drops on the walls, he considers the latter to be clean; the volume of the vessel is independent of the cleaning process used so long as the surface is not injured. (On the other hand, for many microanalytical purposes the walls should also be chemically clean, that is, free from traces of adsorbed acid, alkali, metal oxides, etc.) Contamination of the surface by grease is shown by patches which do not remain wet after a short drainage period, with occasional drops of liquid between. Vessels in this condition generally deliver a volume which is somewhat too large.

Well-known cleaning agents include acetone, alcohol, ether, strong acids, alcoholic alkalies, soap suds, trisodium phosphate, and the so-called synthetic detergents. Traditional in many laboratories is the use of 10% potassium dichromate in concentrated sulfuric acid, but prolonged treatment with this is not recommended by manufacturers of volumetric glassware. Horst[2] removes grease by allowing the vessel to stand for half an hour in contact with sodium permanganate solution weakly acidified with sulfuric acid. Ponndorf[3] recommends 50% potassium hydroxide as a stable and generally useful reagent, though it would seem too drastic for more than a brief treatment. Neutral permanganate solution left in the flask for some time is effective; manganese dioxide separates on the walls, especially on the greasy spots, and after a water rinse is removed by treatment with hydrochloric acid. Chlorine which is liberated aids in the cleaning. The use of 1% hydrofluoric acid has been suggested because of its quick action, but it will dissolve an appreciable quantity of glass if left in contact for more than a very few minutes.

---

[1] W. Schloesser, *Z. angew. Chem.*, **16**, 953, 977, 1004 (1903).

[2] F. W. Horst, *Chem.-Ztg.*, **45**, 604 (1921).

[3] W. Ponndorf, *Z. anal. Chem.*, **84**, 289 (1931).

In general the treatment should be as mild as possible and should be chosen to suit the type of contamination present. It is usually better, for example, to dissolve out most of the grease with an organic solvent such as acetone, then rinse with water, and remove the last trace of film with an oxidizing agent, than to use a longer exposure to the latter only. Whatever method is employed, however, the glassware should at the last be thoroughly rinsed with tap water followed by distilled water.[4]

When uniform drainage is not secured by chemical means, mechanical cleaning may have good effect. Burettes are washed with soap suds and a long-handled brush, flasks with pieces of blotting paper and sand, together with water or soap solution, and pipettes by shaking with strong hot soap suds. Too vigorous mechanical treatment should be avoided because the walls may receive fine scratches which favor contamination.

A thin film of grease is especially stubborn. This may come in part from stopcock lubricant, from reagents, or from the distilled water if the latter is supplied from boiler condensate. The reader is referred to Horst,[2] Berg,[5] or Lowson[6] for discussions of the reasons why glass surfaces become greasy. According to Schloesser[1] some varieties of glass are acted upon by water and become of themselves somewhat dirty. It is desirable to use glassware which is as resistant as possible.

If all the above methods fail or if consideration of catalytically active trace impurities (for example, in work with peroxide solutions) requires especially thorough cleaning, a steaming out of the vessel for several minutes is in order. Disadvantages of the treatment are that the glass suffers some devitrification and that time must be allowed for equalization of thermal effects before the true volume of the vessel is restored. These are offset by the excellent cleaning that can be obtained.

Unpublished experiments by F. W. Power indicate that thermal hysteresis effects may be much smaller than has generally been supposed. In several pieces of glassware which he studied, the changes produced by heating and recooling were negligible for the purposes of volumetric analysis.

---

[4] *Cf.* E. P. Laug, *Ind. Eng. Chem., Anal. Ed.*, **6**, 111 (1932).

[5] R. Berg, *Chem.-Ztg.*, **45**, 749 (1921).

[6] W. Lowson, *Nature*, **121**, 14 (1928).

3. Description of Measuring Vessels.—*Volumetric flasks* are long-necked, wide-bodied vessels which have one or more marking lines around the neck; often they are provided with ground-in stoppers. They serve for the preparation of definite volumes of solution. Ordinarily they are made in sizes of 50, 100, 250, 500, 1000, and 2000 ml. (see Fig. 1). For special purposes there are also flasks in 25, 20, 10, and even 5 ml. sizes in various forms.

The level to which the flask is to be filled is indicated by a mark drawn all the way around the neck so that parallax may be easily avoided. Usually volumetric flasks are marked only "to contain." In general the mark should come far enough below the stopper to give a good-sized air bubble.

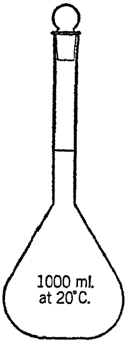

Fig. 1. Volumetric Flask

Flasks which are calibrated for two different volumes, for example, 100 ml. and 110 ml., with one mark for each and with the neck proportioned accordingly, are sometimes used. These are especially convenient if it is desired to treat a measured quantity of liquid with a small amount of reagent and then make up to a definite volume without diluting too much.

The National Bureau of Standards[7] has established the following requirements for the inner diameter of the neck of a flask at the height of the calibration mark:

Capacity, ml.	50	100	250	500	1000	2000
Maximum diam., mm.	10	12	15	18	20	25
Minimum diam., mm.	6	8	10	12	14	18

When a volumetric flask is used for the preparation of a solution of known content, the weighed quantity of material is dissolved in water in the flask. After waiting until the temperature has become equalized, water is allowed to run in to a point a few centimeters below the mark, with swirling to mix the solution. The neck above the mark is then wiped dry with a rolled strip of filter paper and the flask is filled to the mark with water from a wash bottle or capillary pipette with care not to wet the neck again. After filling and stoppering, the flask is shaken vigorously until the contents are thoroughly mixed.

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[7] E. L. Peffer and Grace C. Mulligan, *Testing of Glass Volumetric Apparatus*, Circular C434 of the National Bureau of Standards, Washington, D. C. 1941.

A small volumetric flask for micro work has been designed by Caley[8] in order to overcome the difficulty caused by the trapping of incompletely mixed solution around the stopper, and to permit more rapid mixing. This flask has a mixing chamber above the calibration mark.

Measuring cylinders: Measuring cylinders are fairly wide cylindrical tubes closed at the bottom and generally provided with a thick glass base to increase their steadiness. They are ordinarily made "to contain," but since they are much less exact than flasks, they are to be recommended only for rough measurements.

Pipettes: Pipettes are generally constructed to deliver and are classified as *transfer* pipettes and *measuring* pipettes.

Transfer pipettes have only a single mark for measuring a definite volume of liquid, and are blown in various shapes. Those most commonly used are glass tubes, each expanded spherically or cylindrically in its middle portion, drawn out at the bottom to a tip, and carrying a calibration mark on the narrow neck above. In general the inner diameter of the narrow tube should not exceed 6 mm., the minimum distance of the mark from the enlarged portion should be 10 mm., and the minimum distance to the upper end of the suction tube should be 110 mm.

The latter distance is intentionally chosen so large because in filling the pipette the liquid must be brought above the mark. The upper opening is then closed, ordinarily with the index finger, the outside of the tip is wiped dry with a cloth or filter paper, and by careful admission of air the meniscus of the liquid is allowed to fall to the mark. The tip of the index finger should be somewhat moist to control the flow, but not so wet that a troublesome film of liquid forms.

In filling the pipette one should not apply suction too vigorously because bubbles may appear on the surface and render an exact reading impossible. It is then necessary either to wait until they break, which for certain solutions may take a long time, or to drain the pipette, blow out the bubbles, and start over again. Another probable consequence of applying too strong suction by mouth is the introduction of saliva into the tube. In pipetting corrosive or poisonous liquids it is advisable to use a rubber bulb, or a suction pump with the protection of a trap in case too much liquid is drawn up. If the liquid is very volatile, it is better to fill the pipette by pressure.

---

[8] E. R. Caley, *Ind. Eng. Chem., Anal. Ed.*, **13**, 204 (1941).

Pipettes can be emptied in various ways:

(*a*) By free outflow only—the pipette, held in a vertical position, is allowed to discharge without touching the wall of the receiving vessel.

(*b*) By free outflow (as in *a*) and touching the tip to the glass wall after discharge, to remove the last drop.

(*c*) By free discharge and blowing out of the last drop.

(*d*) By outflow with continuous resting of the tip of the pipette against the wall of the vessel.

The quantity of liquid delivered from a pipette varies slightly according to the manner of emptying. A pipette must always be used in the way for which it was calibrated. For pipetting into a dry vessel the following method is said by Wagner[9] to give the most exact results: The contents are allowed to run out freely, then the surface of the liquid is touched with the tip of the pipette.

In practice, method (*d*) has proved good. The pipette is filled with liquid, the discharge tip is dried with cloth or filter paper, and the liquid is carefully allowed to run down to the mark, the tip being held against the wall of the vessel from which the solution has been taken. Then with the pipette held vertically, its tip resting against the wall of the receiving vessel, the liquid is allowed to discharge. When the continuous flow has ceased, the tip is again touched to the glass after 15 seconds if no time is specified, otherwise after the interval that is given.[10] Generally pipettes manufactured in the United States are calibrated for direct delivery with no drainage interval.

Only in using Stas pipettes is the method (*a*) of free outflow to be recommended. A Stas pipette[11] terminates in a straight drawn capillary tube that is cut off flat. The liquid runs out in a rapid stream and then stops suddenly. Subsequent drops due to drainage are not collected.

Method (*b*) is essentially the one practiced in the Bureau of Standards calibrations.[7]

Method (*c*) involving the blowing out of the last drop is the least exact. Graduated pipettes are sometimes calibrated in this manner.

In emptying a pipette, a quantity of liquid runs out after the end of the free flow; the amount is smaller the longer the discharge itself has lasted. Naturally the delivery of the pipette varies according to whether these drainings are included or not. The drainage can be kept very small by a sufficiently long outflow time. Thus Wagner[11a] found for a 50 ml. pipette a drainage error of 0.013% after waiting one minute; the time of outflow in this case amounted to 87 seconds, which is abundantly long for laboratory practice.

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[9] J. Wagner, *Massanalytische Studien*, Dissertation, Leipzig 1898, p. 17; *Z. physik. Chem.*, **28**, 193 (1899).

[10] *Cf.* W. Schloesser, *Z. angew. Chem.*, **16**, 953, 997, 1004 (1904).

[11] J. S. Stas, *Oeuvres completes*, Vol. I, p. 830; *Ann. chim. phys.*, **25**, 89 (1872).

According to Ponndorf[12] one should be careful not to move the pipette during the discharge. With care he could obtain results consistent to within 0.01–0.02%, whereas with much motion of the pipette variations of 0.05–0.07% were encountered. Ponndorf concurs with Wagner that an outflow time of about 90 seconds is best.

In general the tips of transfer pipettes should be of such dimensions that the free outflow lasts not more than one minute and not less than the following for the respective sizes:

Capacity, ml.	5	10	50	100	200
Minimum outflow period, sec.	15	20	30	40	50

Under these conditions the drainage is practically negligible if one waits 15 seconds after the outflow before taking off the last drop.

The investigations of Wagner[12a] show that the "wetting error" for ordinary volumetric solutions is practically the same as for water. Even a normal sodium carbonate solution does not deviate seriously. However, if instead of working with dilute aqueous solutions one deals with concentrated sulfuric acid, alcoholic solutions, or in general with solutions that have surface tensions and viscosities appreciably different from those of water, the drainage and wetting errors have to be determined experimentally for each particular case.[13]

Both of these errors can be eliminated by using pipettes calibrated "to contain" and washing them out quantitatively with water or the solvent in question, after emptying. Ponndorf[12] used pipettes of this type (*Nachwaschpipetten*) in his exact titrations. Obviously they are not to be recommended for ordinary practical purposes. Though the same pipette might be used both "to contain" and "to deliver" if appropriately marked, the two marks could easily cause confusion.

In working with identical solutions, the quantities delivered by a Stas pipette (*cf.* above) are remarkably uniform. Hoitsema[14] found that the usual procedure of free discharge has under good conditions an inherent uncertainty of ±5 mg. for a 100 ml. pipette, or 0.005%. This amount can even be reduced to 2–3 mg. with special precautions.

[11a] J. Wagner, *loc. cit.*, p. 22.

[12] W. Ponndorf, *Z. anal. Chem.*, **84**, 289 (1931); **85**, 1 (1931).

[12a] J. Wagner, *loc. cit.*, p. 13.

[13] W. Schloesser and C. Grimm, *Chem.-Ztg.*, **30**, 1070 (1906).

[14] C. Hoitsema, *Z. angew. Chem.*, **17**, 648 (1904).

Smaller Stas pipettes are not recommended for analytical practice because the drainage error varies greatly for different liquids.

In the course of time there have been devised various forms of automatic transfer pipettes which afford good service in routine work. The reader is referred to Beckurts[15] for details.

Measuring pipettes are cylindrical glass tubes with scale divisions, numbered from top to bottom, conforming to the capacity. At the bottom they are drawn out to a tip as are transfer pipettes, and the larger ones (5 ml. or more) are also constricted at the top. They serve for measuring any desired volume of liquid, generally where exactness is not essential.

Burettes: Burettes are cylindrical glass tubes provided with a graduation numbered from top to bottom; at the bottom they are closed by means of either a glass stopcock or a rubber tube with pinchcock or glass bead. The capacity is generally 50 ml., though burettes of 25 and 100 ml. are available. For working conveniently with fairly large volumes, one may choose a 60 ml. burette.

For semimicro and micro work there are burettes of 10, 5, 2, or 1 ml., graduated to 0.01 ml.[16] A piece of apparatus for measuring macro quantities of liquid with the accuracy of a microburette has been devised by Eissner.[17] It makes use of a special macroburette with constrictions at the marks for 0, 3, 6, 9, 12 and 15 ml., so that at these points the diameter is the same as that of a parallel microburette to which connection is made at the bottom, through a three-way stopcock. The microburette has a capacity of 3 ml. and is graduated in hundredths. In titrating, both burettes are filled to the zero marks and solution is delivered from the larger until the end-point is observed. Then liquid from the smaller is forced back into the larger by pressure from a hand bulb, until the level reaches the next mark above. Both burettes are read, the sum representing the volume used in titration.

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[15] H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig 1913, pp. 17–19.

[16] For microburettes without stopcocks, see: E. Schilow, *Z. angew. Chem.*, **39**, 232, 582 (1926); *Z. anal. Chem.*, **70**, 23, 35 (1927); R. Flatt, *Helv. Chim. Acta*, **17**, 1513 (1934).

Microburettes and micropipettes are described by: O. Folin, *J. Biol. Chem.*, **21**, 198 (1915); D. D. Van Slyke and J. M. Neill, *ibid.*, **61**, 532 (1924); A. Benedetti-Pichler, *Z. anal. Chem.*, **73**, 200 (1928); A. F. Shohl, *J. Am. Chem. Soc.*, **50**, 417 (1928). Complete descriptions of apparatus for microvolumetric analysis are given in the monograph of J. Mika, *Die exakten Methoden der Mikromassanalyse*, Enke, Stuttgart 1939, and in an article by G. H. Wyatt, *Analyst*, **69**, 81 (1944). See also A. A. Benedetti-Pichler, *Introduction to Microtechnique of Inorganic Analysis*, Wiley, New York 1942, pp. 234–260.

[17] W. Eissner, *Z. anal. Chem.*, **91**, 172 (1932). See also W. M. Thornton, Jr., *Ind. Eng. Chem. Anal. Ed.*, **16**, 50 (1944).

Burettes, like pipettes, are used "to deliver," so that drainage and wetting errors have to be considered. There are two methods of obtaining reproducible readings. One may either allow sufficient time after the initial outflow for drainage to take place completely, or adjust the outflow to such a slow rate that no perceptible drainage follows. In the latter case, both the drainage and the amount of liquid remaining on the walls decrease toward a limit as the delivery period is lengthened. With a given opening, the rate of delivery varies with the height of liquid in the burette, as a result of the changing hydrostatic pressure.[18] The residual liquid adhering to the wall is also a function of the burette diameter. The smaller the latter, the larger is the ratio between the quantity remaining and the quantity delivered.

Wagner recommended the use of a tip from which the outflow is slow enough so that the drainage becomes negligible. In his experiments the outflow of a 40 ml. burette required 50 seconds. On the contrary, Schloesser said that a 10 minute delivery period is necessary though for practical purposes two minutes are sufficient. He found also that the customary standard solutions have the same drainage characteristics as water.

The Bureau of Standards specifies that the outflow rate of burettes and measuring pipettes be restricted by the size of the tip and that for any graduated interval the time of free outflow must be not more than three minutes nor less than the following, for the respective lengths:

MINIMUM OUTFLOW TIME FOR BURETTES AND PIPETTES

Length Graduated, cm.	Minimum Outflow Time, sec.	Length Graduated, cm.	Minimum Outflow Time, sec.
70	160	40	70
65	140	35	60
60	120	30	50
55	105	25	40
50	90	20	35
45	80	15	30

An outflow time of one minute for each 10 ml. of liquid has proved practically useful. According to Schoorl it is then superfluous to wait for drainage. Very exact investigations of Lindner and Haslwanter[19] have almost completely confirmed this statement. Of all the listed methods of emptying burettes, that of Schoorl gives the smallest drainage error. It is clearly shown by the work of Lindner and Haslwanter that increasing the outflow time results in a marked decrease in the amount of liquid adhering to the glass walls, as well as a decrease in any further drainage. Also, drainage does not commence immediately after outflow of the bulk of the liquid; the time before onset of drainage increases with increase in the outflow time.

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[18] *Cf.* especially W. Schloesser, *Chem.-Ztg.*, **28**, 6 (1904).

The following tables, taken from the work of Lindner and Haslwanter,[19] are instructive:

DRAINAGE IN CUBIC MILLIMETERS FOR A FIFTY MILLILITER BURETTE AT ROOM TEMPERATURE

Drainage Time, min.	Outflow Time							
	18 sec.	40 sec.	1 min.	2 min.	4 min.	6 min.	8 min.	10 min.
0.5	0							
1.0	7	0						
1.5	41		0					
2.0	78	1						
3.0	130	7	3					
5.0	182	40	24	0				
10.0	235	94	53	6	0			
20.0	273	132	81	31	8	4	1	0
60.0	311	170	112	58	35	23	13	7
240.0	339	198	140	85	61	47	36	28

DRAINAGE IN CUBIC MILLIMETERS FOR A TEN MILLILITER BURETTE AT ROOM TEMPERATURE

Drainage Time, min.	Outflow Time						
	18 sec.	40 sec.	1 min.	2 min.	4 min.	6 min.	10 min.
0.5	0.0						
1.0	1.1	0.0					
1.5	3.7	0.2	0.0				
2.0	10.2	1.1	0.0				
3.0	22.6	5.5	0.3	0.0			
5.0	38.7	11.9	1.9	0.2			
10.0	54.9	25.5	8.7	2.2	0.0		
20.0	66.5	36.6	19.7	8.8	0.7	0.2	0.0
60.0	78.0	47.6	30.7	19.4	7.1	4.3	2.6
240.0	85.5	55.2	38.2	27.0	14.6	11.4	7.4

The drainage time is measured from the beginning of outflow and therefore represents the total time elapsed for a titration. An increasingly strong influence of drainage occurs chiefly with burettes of smaller content (that is, those of narrower bore). With typical 0.1 N solutions Lindner and Haslwanter obtained about the same values as with water. The drainage error is independent of temperature over a fairly wide range.

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[19] J. Lindner and F. Haslwanter, *Z. angew. Chem.*, **42**, 821 (1929).

Burette Stopcocks; Systems for Excluding Air: Burettes may be provided with either glass stopcocks or pinchcocks. Those with glass stopcocks are useful for all liquids even though the cock is lubricated with vaseline or stopcock grease (mixture of lanolin and wax). According to the investigations of Lunge[20] the action of 0.1 N iodine or permanganate on the grease may be neglected.

Glass stopcocks require frequent attention because they often fail to close tightly. If the tap is too loose the stopcock no longer holds perfectly; if too tight, it is difficult to turn and becomes cemented, especially with alkalies, so that it can be loosened only with difficulty. For routine use with alkalies, therefore, burettes having stopcocks of nickel or other resistant metal are desirable. Then there is no longer any danger of glass cementing to glass. If the tap sticks it may ordinarily be loosened with a drop of water. It is much more difficult to loosen in the case of a glass cock; generally careful tapping at the right spot or soaking the stopcock in warm light oil will help, but occasionally the glass breaks and a new stopcock must be sealed on. A device which exerts pressure at the small end of the tap, while the stopcock is held in hot water, is useful in stubborn cases.

Burettes with pinchcocks have a bulge at the bottom for connection through a short rubber tube to a glass delivery tip. In titrations of hot liquids (for example, titration at boiling temperature with rosolic acid indicator) the use of an extension tube bent twice at right angles is desirable to avoid exposure of the whole burette to heating, which would make the reading erroneous. The rubber tube is generally closed by a spring pinchcock. For special purposes a screw clamp may be chosen in order to vary the speed of outflow conveniently. Bunsen's simple and practical method of closing by a suitably rounded piece of glass in the rubber tube is frequently used. Details regarding it are to be found in Beckurts.[21]

According to Schloesser,[18] burettes with pinchcocks have the disadvantage that the tube is dilated by the hydrostatic pressure to different extents at the beginning and end of the emptying process. The magnitude of the error is small; it depends on the length and elasticity of the rubber tube. In order to obtain concordant readings an elastic tube as strong-walled as possible, but not too long, should be selected. The pinch clamp should be applied close to the burette and always at the same place. Lunge^{20} established that a 0.1 N, or even a 0.01 N, iodine solution strongly attacks the rubber and thus loses appreciably in titer, while on the other hand 0.1 N permanganate does not attack rubber seriously.

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[20] G. Lunge, *Z. angew. Chem.*, **17**, 197 (1904).

[21] H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig 1913, p. 24. See also P. Fuchs, *Z. anal. Chem.*, **76**, 166 (1929); **96**, 101 (1934).

Burettes are always set up in a vertical position. Practical details, including a description of automatic filling devices, are given by Beckurts.^{21a}

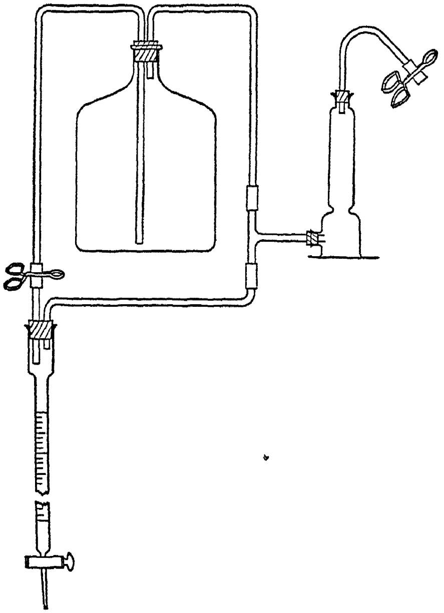

Fig. 2

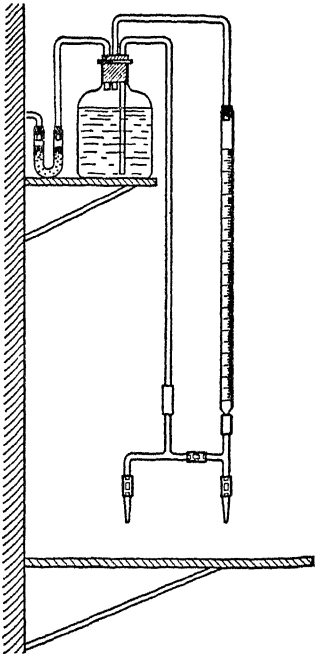

Fig. 3

Burette Systems

In order to avoid evaporation of the liquid, an ordinary burette may be closed by an inverted vial or test tube. This expedient is not sufficient for alkaline liquids, especially hydroxides. The entrance of carbon dioxide should be prevented by a properly mounted soda-lime tube.

Since the alkali may quickly take up carbon dioxide from the air during the filling of the burette, it is desirable to connect the latter with the stock bottle in such a way that exposure to the air is avoided. See Figures 2 and 3.

[21a] H. Beckurts, *loc. cit.*, pp. 27-38.

Such a device is also very well adapted to the use of powerful reducing liquids such as titanous solutions, stannous chloride, vanadous solutions, etc. In this case a Kipp apparatus is put in place of the soda-lime tube and an indifferent gas such as hydrogen or carbon dioxide is kept in contact with the liquid.

Reading of Burettes and Other Volumetric Apparatus: In reading a measuring vessel, the surface of the liquid is compared with a mark at the same height or with a corresponding subdivision. In a relatively narrow tube or the neck of a flask, the liquid surface is not plane but is curved as a result of surface tension. The bottom of this *meniscus* is usually selected as the level to be read. Only with highly colored liquids such as 0.1 N permanganate should the reading be referred to the top rim of the liquid surface. The exact recognition of the bottom of the meniscus is made difficult by reflection phenomena. Furthermore an error due to parallax is introduced if the eye is not at exactly the same height as the surface of the solution. Parallax errors are easily avoided in vessels whose marks completely encircle the tube or neck.

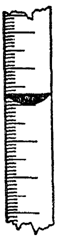

Fig. 4

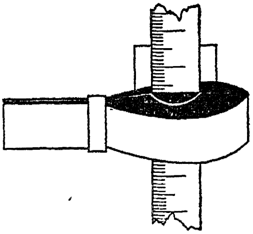

Fig. 5

Reading of Burettes

The Bergmann-Göckel screen is recommended widely as a reading aid; it is a wooden clamp, the upper edge of which is dull black, and to which[22] a piece of white paper may be fastened. Since a common test tube holder is suitable for use with flasks and burettes of ordinary diameter, such a device may be made without difficulty or expense. Figure 4 shows the reading without a clamp, Figure 5 with clamp and white paper.

The simplest—and perhaps best—reading device is a piece of pasteboard that has a white and black field with a straight-line boundary between (a black sheet pasted on a white background). This little card is held in back of the burette with the black surface down so that the horizontal boundary is about 1 mm. below the meniscus. In this way troublesome reflections are completely screened off and a reading free from observational error is assured (see Fig. 6). If desired, two horizontal slits may be made in the card for slipping it over the burette.

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[22] H. Göckel, *Chem.-Ztg.*, **27**, 1036 (1903).

It should be emphasized that all related readings must be made in the same way, since one and the same burette support can permit the finding of somewhat different numerical values depending on the manner of reading. It is only by equalizing such errors of observation that they are cancelled in taking the difference between two readings.

By using a reading diopter in which a hairline scale is so placed that a division of 0.1 ml. on the burette is subdivided by optical projection into 0.01 ml. divisions, Ponndorf[12] has succeeded in reading to 0.01 ml. directly and estimating to the next smaller order of magnitude. For fine titrations of very great accuracy (to 0.01%) such an instrument is indispensable. That used by Ponndorf was produced by the firm of A. Dargatz in Hamburg.

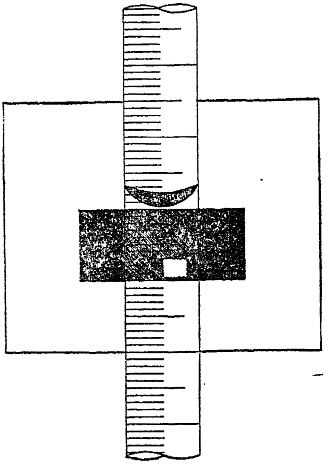

Fig. 6. Reading Burette with Card

Schattenstein[23] recommends the following procedure which makes possible a very accurate reading: A piece of glass tubing (see Fig. 7) about 2 cm. long is placed over the burette so that it can be moved up or down. A very thin ring line is engraved around this tube near the top; below this at a distance of 1 mm. is a wider black line which encircles half the tube. On the other side of the tube directly beneath the ring line are ten division lines which correspond to nine divisions on the burette. A thin paper strip is pasted on the back of the tube. The glass hull is held by a clamp. This device has the advantages that parallax errors are eliminated, that the meniscus is outlined clearly by the black strip, and that the vernier principle can be applied in reading the burette. Obviously the last advantage is lost if the burette does not have a uniform inside diameter (equally spaced divisions).

Schellbach sought to attain accurate and convenient readings by means of a thin dark vertical stripe on a milk glass background on the back wall of the measuring vessel. In this case it is not the bottom rim of the meniscus that is sought, but the point of separation between the reflections of the upper and lower surfaces of the meniscus. When the eye of the observer is at the

[23] A. J. Schattenstein, *Z. anal. Chem.*, **88**, 435 (1932). The method was simultaneously and independently proposed by E. v. Migray, *ibid.*, **88**, 436 (1932).

proper position the stripe appears to be constricted at a sharply defined point. This insures a greater certainty in recognizing the liquid surface but does not guard completely against a parallax error.

Weight Burettes: Errors of drainage, reading, and temperature change are all eliminated if titrations are carried out on a weight basis instead of volumetrically. For this purpose the standard solution is made to contain a certain number of milliequivalents per gram rather than per milliliter and it is delivered from a type of burette which can easily be weighed. Such a vessel is called a weight burette[24]; some typical forms which have been employed are shown in Figures 8 and 9.

Figure 10 is a simple weight burette proposed by Hahn.[25] The air tube *L* is drawn from heavy-walled glass tubing of narrow bore; *S* is a loop by which the burette may be hung on the hook of a balance. The portion of the tube above the broken line is perpendicular to the plane in which the rest of the apparatus lies. *T* is a dropping tube for delivery of the solution At the end of tube *L* is a small nipple closed by a rubber cap such as an ordinary rubber "policeman." In the latter a small hole is punched; by closing the hole and squeezing the rubber, one can force solution out from *T* drop by drop. When the pressure is released, the solution is sucked back slightly and discharge stops at once. The burette is filled through *T* by means of suction applied at *L*.

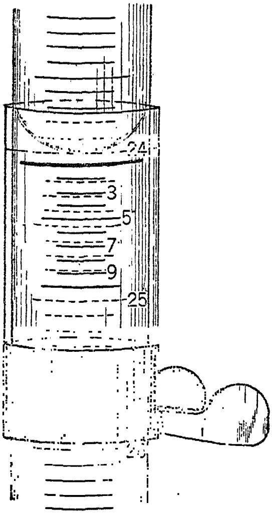

Fig. 7. Reading Device (According to Schattenstein)

LaMer and Friedman[26] recommended a convenient form of weight burette, shown in Figure 11.

In titrating with a weight burette, the burette is filled and weighed, then the titration is carried out to the end-point and the burette is reweighed. The difference in weight gives the quantity of standard solution that was used. According to Incze[24] one can in this way

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[24] See, for example, S. P. L. Sörensen, *Z. anal. Chem.*, **42**, 335 (1903); G. Incze, *ibid.*, **54**, 406 (1915); M. Ripper, *Chem.-Ztg.*, **16**, 794 (1892); E. Lange and E. Schwartz, *Z. Elektrochem.*, **32**, 243 (1926). For micro weight burettes see L. Szebellédy and O. Clauder, *Z. anal. Chem.*, **105**, 26 (1936); B. Ormont, *ibid.*, **75**, 209 (1928).

[25] F. L. Hahn, *Mikrochim. Acta*, **3**, 7 (1938).

[26] V. K. LaMer and H. B. Friedman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 54 (1930).

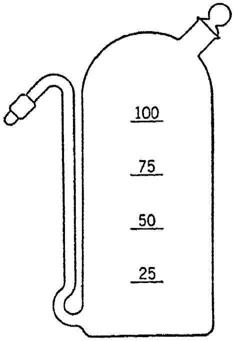

Fig. 8

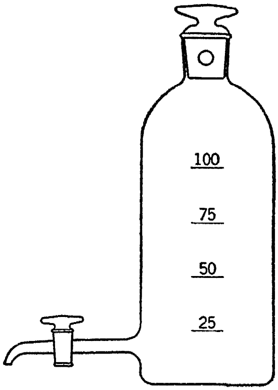

Fig. 9

Weight Burettes

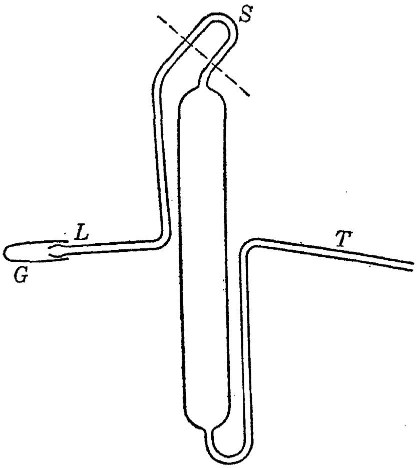

Fig. 10. Weight Burette according to Hahn

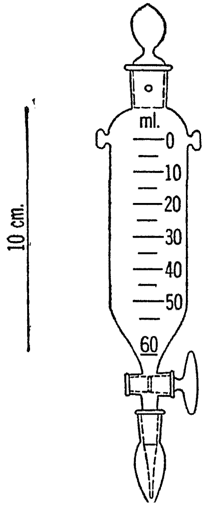

Fig. 11. Weight Burette of LaMer and Friedman

make determinations that are accurate to the fourth decimal place. This corresponds to the error of weighing, for the weighings are naturally made in analytical fashion to the fourth place. Yet such exact weighings have practically no meaning considering the much greater uncertainty which occurs in the determination of the end-point as a result of the drop error. At the end-point of a titration the change can be perceived at best with an accuracy of "a drop," so that usually an excess of standard solution is used which amounts to more than 10 mg. It may be possible to establish experimentally in place of the "titration error," a correction for the excess added, but the perception of color tints by the human eye is still subject to fairly great uncertainty. Therefore it is generally useless to carry out the weighings more accurately than to 10 mg. If more than 10 g. of solution is used the weighing error is then less than 0.1%. When smaller amounts are taken, as in the case of microtitrations, the accuracy of the weighing must be increased proportionately.

The combined use of a weight burette and an ordinary burette is advantageous for exact analytical work. From the former one adds a quantity of solution such that the equivalence-point is almost reached, then the titration is completed with a suitably diluted solution from an ordinary burette. In this way an accuracy of 0.01% can be obtained if the visual end-point coincides with the equivalence-point.

4. Calibration of Volumetric Apparatus.[27]—The legally established unit of volume is the "true liter," that is, the volume occupied by a *mass* of one kilogram of water at the temperature of maximum density (3.98°C.) and under normal atmospheric pressure.[28]

There is a difference between the two volumes, cubic decimeter and liter (or between cubic centimeter and milliliter). The cubic decimeter is derived from the unit of length, while the liter is related to the mass of the standard kilogram of platinum that is kept in Paris. Extensive investigations at the International Bureau of Weights and Measures have shown that the liter is actually about 28 cu. mm. larger than the cubic decimeter. For most purposes this difference of about 3 parts per 100,000 is negligible. In principle it is more correct to use the milliliter (ml.) for a unit, as is customary in the United States, than to express fractions of a liter in terms of cubic centimeters (cc.).

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[27] A good compilation on this subject is given in the monograph of V. Stott, *Volumetric Glassware*, Witherby, London 1928. See also J. J. Moran, *Proc. Am. Soc. Testing Materials*, **41**, 492 (1941).

[28] *Travaux et mémoires du Bureau International des Poids et Mesures*, Vol. XII (1902). The pressure is specified because of the compressibility of water; the term "mass," of course, indicates that the weight of water is expressed on the *in vacuo* basis.

In contrast to the true liter, the "Mohr liter" represents the volume that one kilogram of water, at any definite convenient temperature, weighed in air with brass weights, occupies in a vessel of the same temperature. Usually the Mohr liter is related to water at 17.5°C.; it is then 2.3 ml. larger than the true liter. The Mohr liter varies with the density of air, hence the contents of two Mohr liter flasks may differ materially if one of them is calibrated at an appreciably different barometric pressure than the other.

At present only the "true liter" has significance as a unit of volume. Its advantages over the Mohr liter[29] will not be elaborated further.

Whenever the liter is mentioned in the following pages it is to be understood that the "true liter" is meant. A liter flask then contains, when filled to the mark, the volume that 1 kg. of water at 3.98°C., weighed in vacuo, occupies at normal atmospheric pressure. Practically, one cannot weigh 1 kg. of water at that temperature in vacuo in order to calibrate a flask. Instead, 20° is taken as the international normal temperature, and the following derivations are so based. Thus in order to calibrate a liter flask one should weigh (in a vacuum) 1 kg. of water at 3.98° into a flask which has a temperature of 20°. This is experimentally impossible. However, by taking into consideration the specific gravities of water, air and the brass weights, and the cubical expansion of glass, it is possible to calculate how many grams of water have to be weighed at temperature $t°$ in order to make the content of the vessel exactly one liter (or a fraction thereof).

If the relative density of water at $t°$ is s, then one liter in vacuo weighs $s \times 1000$ g.

Since the density of water decreases with rising temperature above 4°C., s becomes less than unity. In a space free of air, not 1000 g. but $1000 \times s$ g. should be weighed. Let a represent the difference $(1000 - 1000s)$.

The weighings are actually made in air, not in a vacuum. Upon weighing in air, one liter of water loses the weight of air which it displaces less the weight of air displaced by the brass weights.

The weight, λ_t, of a liter of air at $t°$ and at a barometric pressure of 760 mm. is:

$$\lambda_t = \frac{1.293052}{1+\frac{1}{273}t} = \frac{1.293052}{1+0.00367t}$$

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[29] *Cf.* especially W. Schloesser, *Z. angew. Chem.*, **16**, 975–977 (1903).

If the specific gravity of the brass weights is taken as 8.4 and if $\{1000 - (a + b + c)\}$ g. of water are weighed into the flask (see below), the correction b for the buoyant effect of air amounts to:

$$b = \left\{1000 - \frac{1000 - (a + b + c)}{8.4}\right\} \lambda t$$

Thus, in taking account of the density of water and the buoyant effect of air, $1000 - (a + b)$ g. of water must be weighed to define the volume of one liter at $t°$ in the flask, and the flask must be at a temperature of $t°$. The flask should not contain one liter at $t°$ but at the normal temperature of 20°C. If, for example, the flask contains exactly one liter at 25°, and if only the glass is cooled to 20° (hypothetical process) without the water changing its temperature of 25°, then if the flask is filled to the mark that is correct at 25°, it will contain less than one liter at 20° because of contraction.

Hence the amount of water weighed in at 25° must be as much more as corresponds to the contraction of the glass between 25° and 20°. Conversely, at a calibration temperature $t°$ that is below 20°, as much less water must be weighed in as corresponds to the expansion of the glass between $t°$ and 20°.

The average coefficient of cubical expansion of glass is 0.000025 per degree centigrade. If the calibration takes place at a temperature $t°$, the correction c for the expansion of glass in weighing one liter is:

$$c = 1000\ (20° - t°)\ 0.000025 \text{ g.}$$

i.e., 25 mg. per degree.

Therefore, at a temperature $t°$, the amount of water which must be weighed into a liter flask in order that its content shall be one liter at 20°C. is:

$$1000 - (a + b + c) \text{ g.}$$

It should be noted that c is positive when t is less than 20° and negative at higher temperatures.

The following table combines all of the values for temperatures between 15° and 35°C. The first column gives the working temperature $t°$, the second the relative density s, of water according to Thiesen, Scheel, and Diesselhorst.[30] The third column lists corresponding values of correction a in milligrams:

$$a = (1000 - 1000s) \times 1000$$

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[30] M. Thiesen, K. Scheel, and H. Diesselhorst, *Wiss. Abhandl. physik.-tech. Reichsanstalt*, **4**, 32 (1904).

VOLUME CALIBRATION

Temp., °C.	s, g./ml.	a, mg.	b, mg.	c, mg.	$\frac{a+b+c}{1000}$
15	0.99913	870	1074	125	2.069
16	0.99897	1030	1070	100	2.200
17	0.99880	1200	1066	75	2.341
18	0.99862	1380	1062	50	2.492
19	0.99843	1570	1058	25	2.653
20	0.99823	1770	1054	0	2.824
21	0.99802	1980	1050	−25	3.005
22	0.99780	2200	1046	−50	3.196
23	0.99757	2430	1042	−75	3.397
24	0.99733	2670	1038	−100	3.608
25	0.99708	2920	1034	−125	3.829
26	0.99682	3180	1030	−150	4.060
27	0.99655	3450	1026	−175	4.301
28	0.99627	3730	1022	−200	4.552
29	0.99598	4020	1018	−225	4.813
30	0.99568	4320	1014	−250	5.084
31	0.99537	4630	1010	−275	5.365
32	0.99505	4950	1006	−300	5.656
33	0.99473	5270	1002	−325	5.947
34	0.99440	5600	998	−350	6.248
35	0.99406	5940	994	−375	6.559

The fourth column contains, also in milligrams, the correction b for the buoyant effect of air. The values apply for a barometric reading of 760 mm. and an average degree of saturation by water vapor of 50%. For a barometer reading B, b must be corrected as follows:

$$b' = (B/760)b$$

It can be calculated that in the temperature range 15° to 35° there is an average change of 14 mg. in b for a 10 mm. barometric difference, and b is larger when the barometer reads higher than 760. In general b' may be calculated from the expression:

$$b' = b + (B - 760)1.4 \text{ mg.}$$

For most purposes the moisture content of the air may be completely ignored.

If the temperature of the water ($t°$) is different from that of the air ($t_1°$), b is about 4 mg. larger for each degree that t_1 is smaller than t, and vice versa; therefore:

$$\Sigma b = b + 1.4(B - 760) + 4(t_1 - t)$$

In the fifth column is listed the correction c for expansion of glass between t° and 20°. The last column shows the total correction expressed in grams, that is, $(a + b + c)/1000$.

The quantity G_t represents the number of grams of water which should be taken at t° in order to calibrate a one liter flask for a normal temperature of 20°C. This is equal to:

$$G_t = 1000 - \frac{(a + b + c)}{1000}$$

Illustration: Assume a temperature of 25°C. and a barometric reading of 760 mm. The weight of water to be taken in calibrating a one liter flask to be exact at a normal temperature of 20° is then:

$$1000 - 3.83 = 996.17 \text{ g.}$$

If the water is at 25°, the air at 26°, and the pressure 740 mm., then:

$$\Sigma\, b = 1034 - 28 - 4 = 1002$$

$$\frac{a + b + c}{1000} \quad 3.80$$

$$1000 - 3.80 = 996.20 \text{ g.}$$

The error caused here by neglecting the barometric deviation and the air temperature would amount only to 0.03 g., or 3 parts per 100,000 (0.003%) which is insignificant.

If the normal temperature is to be other than 20°C., the value of $(a + b + c)$ should be increased by 25 mg. for each degree above 20°, or diminished by the same amount for each degree below. For example, to make the vessel accurate at 25°, 125 mg. should be added to $(a + b + c)$.

5. Practical Performance of Calibrations.—Measuring vessels of very good quality are available on the market. Those conforming to the required specifications may be sent to the United States Bureau of Standards for certification.[31] Nevertheless it is desirable for the chemist to calibrate his own volumetric apparatus, or to test its correctness if already calibrated.

General Rules: Vessels and auxiliary apparatus before weighing must be fully dry and, like the water used for testing, should have remained a long time in the testing room in order to reach temperature equilibrium with the air. The vessels must be clean (free from grease) and should be handled as little as possible. The temperature of the water and air is determined with an accurate thermometer.

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[31] See National Bureau of Standards Circular C434 mentioned on page 6.

During filling to the mark and reading, parallax is avoided by having one's eye at such a level that the portion of the mark on the back coincides with that on the front (*cf.* p. 15). The level of the liquid is read at the height of the bottom point of the meniscus with the vessel in a vertical position.

Specific Details: (*a*) *Volumetric flasks:* Place the dry vessel and its nominal weight, that is, 1000 g. for a one liter flask, on the right hand pan of a suitable balance, and tare. Then remove the nominal weight and in its place put $(a + b + c)/1000$ grams (see table, p. 22). Equilibrium is again established by pouring water into the flask. Care should be taken that no drops remain clinging to the neck of the flask above the surface of the water, but if any drops appear they are removed carefully by touching them with a rolled strip of filter paper. The last exact adjustments are made by adding or removing a few drops of water with a capillary tube or pipette. As soon as the pans balance exactly, the flask is placed on a level surface and a strip of paper with a straight edge is pasted around the neck so that the top of the paper is even with the bottom of the meniscus. A small mirror may be used advantageously to avoid a parallax error. The paper may then be lacquered or the flask may be marked permanently with a scratched, or better, etched line. Details of the etching procedure are given in various texts.[32]

A similar procedure is followed in testing a flask which has already been calibrated. The empty flask plus its nominal weight is tared, the weight is removed and $(a + b + c)/1000$ grams are added, then the flask is filled to the mark. If equilibrium is not established, the weight that is found necessary to restore balance is taken as the correction to be applied.

The Bureau of Standards has set the following tolerances for volumetric

Nominal volume, ml....	50	100	250	500	1000	2000
Limit of error, ml......	0.05	0.08	0.11	0.15	0.30	0.50
Limit of error, %......	0.1	0.08	0.044	0.03	0.03	0.025

(*b*) *Transfer pipettes:* If the pipette already has a mark, it may be tested for accuracy and used with a correction if necessary, or a new mark may be made at the proper position. In testing the correctness of the original mark, the pipette is filled with water of known temperature and is drained into a tared flask in accordance with the directions given under method (*d*) p. 8. With the aid of the table on p. 22, the volume of water delivered at the normal temperature is calculated from the observed weight. This is recorded and a corresponding label is affixed to the pipette.

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[32] For example, F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, Vol. II, 9th edition, Wiley, New York 1942, p. 442.

To make a new mark in order that the pipette shall deliver exactly the nominal quantity, a narrow strip of millimeter cross-section paper is pasted along the axis of the suction tube and the position of the mark is located roughly by sucking the desired volume from a measuring cylinder. The level of the meniscus is marked on the paper, then the water is allowed to flow into a tared vessel. If the pipette should deliver v ml., the weight of water flowing out at $t°$ should amount to $v - [(a + b + c)/1000] \times v/1000$ grams.

Obviously the first determination is only approximate. From the difference between the weights of water desired and observed, the error can be found, and from this the distance between the temporary mark and the correct one may be calculated if the inner diameter of the tube is known. The latter can be determined with a metal wedge. In the table below (suggested by Professor Schoorl of Utrecht), the heights corresponding to a volume of one ml. are shown for various diameters of tubing. The new mark is placed at the calculated distance from the old and the pipette is filled and tested again in the proper manner. In this way the correct position of the mark may be located quite exactly.

HEIGHT OF A ONE MILLILITER CYLINDRICAL TUBE OF GIVEN DIAMETER

Inside Diameter, mm.	Height Corresponding to 1 ml. Volume, mm.	Inside Diameter, mm.	Height Corresponding to 1 ml. Volume, mm.
2.0	318	6.0	35.4
2.5	204	6.5	30.2
3.0	141	7.0	26.0
3.5	104	7.5	22.6
4.0	79	8.0	19.9
4.5	63	9.0	15.7
5.0	51	10.0	12.7
5.5	42		

In general the mark should be so placed that the error obtained is less than three-fourths of that allowed by the Bureau of Standards, as shown in the following table:

Nominal volume, ml....	2	5	10	25	50	100
Limit of error, ml.......	0.006	0.01	0.02	0.025	0.05	0.08
Limit of error, %.......	0.3	0.2	0.2	0.1	0.1	0.08

From these tolerances it follows that small pipettes are relatively less accurate and that for exact work it is advisable to use pipettes containing 25 ml. or more.

(*c*) *Burettes:* According to recommendations of the Bureau of Standards, a burette to be tested should be filled to the zero mark, the interval under test emptied by free outflow into a tared flask, and the reading taken after 10 seconds. Burettes to be tested by this procedure are expected to have an outflow time great enough so that the after-drainage is negligible. In general it would seem better to open the stopcock only part way, so that the outflow rate corresponds more nearly to the rate normally prevailing during a titration. Thus it has been recommended[33] that a period of 30 seconds be required for delivery of 5 ml. and that the level of the meniscus be read 30 seconds after the end of delivery.

In either case the burette is clamped in a vertical position and is filled to about 5 mm. above the zero mark. After allowing one minute for drainage from the upper part of the burette, the water is run down exactly to the mark and the tip is touched to a glass vessel for removal of the last drop. Then the interval to be tested is drained under the chosen conditions, the tip is wiped against the inner wall of the tared stoppered flask, and the volume of water delivered is calculated from its weight (*cf.* p. 22).

For ordinary burettes, one tests the intervals 0–5 ml., 0–10, 0–15, etc., up to 50 ml., repeating each until the weighings for a given interval agree to within 10 mg. The burette readings are made to the nearest 0.01 ml.

There is no purpose in testing larger intervals by adding together the results for smaller intervals. As Schloesser[29] has mentioned, the observational error is the same for each individual determination and under these conditions the uncertainty in the final result is as many times that of the direct determination of the volume as there are individual intervals tested.

If the burette differs more than 0.01 ml. from the nominal volume at any point, a correction should be applied to the readings. Each burette is provided with a correspondingly numbered correction card, which is conveniently divided into two columns. On the right are entered the nominal volumes, as 5, 10, 15 ml., and on the left the corrected volumes. Such a card may well be placed on the stand of the burette in question.

The Bureau of Standards permits the following maximum deviations for burettes:

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[33] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 2nd edition, Macmillan, New York 1943, p. 535.

Nominal volume, ml	5	10	50	100
Limit of error, ml	0.01	0.02	0.05	0.10
Limit of error, %	0.2	0.2	0.1	0.1

According to Schloesser,[29] the calibration of burettes with an Ostwald pipette[34] is not to be recommended.

6. Normal Temperature of Measuring Vessels and Temperature during Use.—Vessels are currently calibrated for a normal temperature of 20°C. Usually the temperature deviates from the normal temperature, giving rise to two questions that are important in volumetric practice:

(1) What is the true volume at $t°$ of a standard solution prepared at this temperature in a flask calibrated at 20°?

(2) What volume will the same solution occupy at 20°?

These questions are encountered when one wishes to prepare a solution of exactly known content from a weighed quantity of a primary standard. If the flask has a volume of v_n at the normal temperature, it will have a larger volume at $t°$ if t is higher than 20°. If the coefficient of expansion of glass is ϵ, the volume at $t°$ becomes:

$$v_t = v_n\,[1 + \epsilon(t - 20)]$$

This is the true volume sought in (1) above. Now if the solution is cooled to 20°, the volume decreases. Letting α represent the expansion coefficient of the liquid, the volume becomes:

$$v_{20} = v_t\,[1 - \alpha(t - 20)]$$

or approximately:

$$v_{20} = v_n\,[1 + \epsilon(t - 20) - \alpha(t - 20)]$$

Since α is generally greater than ϵ, the result of the cooling will be that the flask is no longer filled to the mark. If the solution has an expansion coefficient equal to that of water, the corrected volume may be found with the aid of the table on p. 22 and the following relationships:

$$\alpha(t - 20) = \frac{a_t - a_{20}}{1{,}000{,}000}$$

$$\epsilon(t - 20) = \frac{-c_t}{1{,}000{,}000}$$

$$v_{20} = v_n - v_n\left[\frac{a_t - a_{20} - c_t}{1{,}000{,}000}\right]$$

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[34] An improvement in the Ostwald pipette has been described by C. W. Foulk, *J. Ind. Eng. Chem.*, **7**, 689 (1915).

Here v_{20} is the volume which the solution would occupy at a normal temperature of 20°C. The titer of the solution may then be corrected accordingly for use at this temperature.

Illustration: 0.1000 mole of silver nitrate is dissolved in water and diluted to the mark at 28° in a one liter flask calibrated at 20°. The volume at 28° is 1000.2 ml., corresponding to a normality of 0.09998. (This emphasizes how small is the error due to the expansion of glass alone.) However, if the solution is cooled to 20°, the volume becomes 998.2 ml. and the normality 0.10018.

Several marks may be made on the flask, for example, one for a working temperature of 15°C. in the sense that the content of the flask filled to the mark at 15° would be exactly one liter if brought to 20°. In this case one would calibrate by weighing in $1000 - [(a + b + c) - (a_{20} - a_{15} - c_{15})]/1000$ grams. Marks may be made in the same way for other working temperatures such as 17°, 25°, etc. Such special calibration marks for different temperatures have a purpose only when burettes and pipettes are used at the normal temperature.

If solutions are prepared at a given temperature and subsequently used in pipettes or burettes at the same temperature, it is superfluous and under some conditions even erroneous to attempt a partial correction. The case is different when a solution of exactly known titer is prepared and is to be used at another temperature. One may, for example, prepare an exactly 0.1 N iodate solution at 20°. If this is used at 26° the volume will have increased by 0.14%, with an equal decrease in titer. This correction has to be considered in exact analyses. Schloesser[35] has prepared a convenient table for this purpose, based on dilatometric measurements of Schulze.[36] In calculating the values for a normal temperature of 20°, Schloesser used 0.000027 as the expansion coefficient of glass.[37]

It follows from his data that the differences between values for water, 0.01 N solutions and 0.1 N hydrochloric acid are so small that the corrections for these liquids may be considered identical. Even other 0.1 N solutions show but slight deviations from these.[38]

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[35] W. Schloesser, *Chem.-Ztg.*, **29**, 510 (1905).

[36] A. Schulze, *Z. anal. Chem.*, **21**, 167 (1882).

[37] Another set of tables was given by Y. Osaka, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **4**, 113 (1920), based on the densities of various standard solutions between 5° and 30° as determined by K. Inamura in 1917. Osaka used 0.000029 as the expansion coefficient of glass.

[38] *Cf.* also N. Schoorl, *Chem. Weekblad*, **23**, 581 (1926). M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **2**, 260 (1930), assembled the values in a diagram from which the required correction for each titration can be read.

CONVERSION OF VOLUMES OF STANDARD SOLUTIONS AT $t°$ TO VOLUMES AT A NORMAL TEMPERATURE OF 20°C.

The numbers give the volumes in ml. by which one liter of solution is larger (+) or smaller (−) when brought from $t°$ to 20°. *Cf.* Schloesser[35] and Schoorl.[38]

Temp., °C.	Water, 0.01 N Solns., 0.1 N HCl	0.1 N Solns.	0.5 N HCl	1.0 N HCl	0.5 N NaOH	1.0 N NaOH
5	+1.5	+1.7	+1.9	+2.3	+2.35	+3.6
6	1.5	1.65	1.85	2.2	2.25	3.4
7	1.4	1.6	1.8	2.15	2.2	3.2
8	1.4	1.55	1.75	2.1	2.15	3.0
9	1.4	1.5	1.7	2.0	2.05	2.7
10	1.3	1.45	1.6	1.9	1.95	2.5
11	1.2	1.35	1.5	1.8	1.8	2.3
12	1.1	1.3	1.4	1.6	1.7	2.0
13	1.0	1.1	1.2	1.4	1.5	1.8
14	0.9	1.0	1.1	1.2	1.3	1.6
15	0.8	0.9	0.9	1.0	1.1	1.3
16	0.6	0.7	0.8	0.8	0.9	1.1
17	0.5	0.6	0.6	0.6	0.7	0.8
18	0.3	0.4	0.4	0.4	0.5	0.6
19	0.2	0.2	0.2	0.2	0.2	0.3
20	0.0	0.0	0.0	0.0	0.0	0.0
21	−0.2	−0.2	−0.2	−0.2	−0.2	−0.3
22	0.4	0.4	0.4	0.5	0.5	0.6
23	0.6	0.6	0.7	0.7	0.8	0.9
24	0.8	0.9	0.9	1.0	1.0	1.2
25	1.0	1.1	1.1	1.2	1.3	1.5
26	1.3	1.4	1.4	1.4	1.5	1.8
27	1.5	1.7	1.7	1.7	1.8	2.1
28	1.8	2.0	2.0	2.0	2.1	2.4
29	2.1	2.3	2.3	2.3	2.4	2.8
30	2.3	2.5	2.5	2.6	2.8	3.2

Illustration: If a 0.1 N silver nitrate solution is prepared at 15°C. in a flask calibrated for 20°, each liter would occupy a volume larger by 0.9 ml. after being brought to 20°.

If 34.75 ml. of 1 N sodium hydroxide has been measured at 25°C. from a burette calibrated for 20°, the corrected volume at the normal temperature is:

$$34.75 - \frac{34.75 \times 1.5}{1000} = 34.75 - 0.05 = 34.70 \text{ ml.}$$

The following table may be used in working with solutions not stronger than 0.1 N:

VOLUME CORRECTION IN MILLILITERS, FOR DILUTE SOLUTIONS USED AT VARIOUS TEMPERATURES

Obs. Vol., ml.	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30°
10	+0.01	+0.01	+0.01	+0.01	0.00	0.00	0.00	−0.01	−0.01	−0.02	−0.02
20	+0.03	+0.02	+0.02	+0.01	+0.01	0.00	−0.01	−0.02	−0.03	−0.03	−0.03
25	+0.03	+0.03	+0.02	+0.02	+0.01	0.00	−0.01	−0.02	−0.03	−0.04	−0.05
30	+0.04	+0.03	+0.03	+0.02	+0.01	0.00	−0.01	−0.02	−0.04	−0.05	−0.07
40	+0.05	+0.04	+0.04	+0.03	+0.01	0.00	−0.02	−0.03	−0.05	−0.07	−0.09
50	+0.06	+0.06	+0.05	+0.03	+0.02	0.00	−0.02	−0.04	−0.06	−0.09	−0.12

CHAPTER II

PRACTICAL PRINCIPLES OF VOLUMETRIC ANALYSIS

1. The Preparation of Standard Solutions.—The preparation of solutions of definite normality is simplest when the substance to be dissolved is available in analytically pure condition and of known formula. By weighing out the equivalent weight or a known fraction of it, dissolving and diluting to a specified volume, one can prepare an accurately standardized solution. Most compounds dissolve with an appreciable energy change—sodium thiosulfate and silver nitrate, for example, absorb heat, and sodium carbonate liberates heat, when dissolved. In these cases the temperature must be equalized with that of the room or with the normal temperature, either by long standing (with frequent agitation) or with the aid of a suitable bath, before the solution is finally diluted to the mark. The last few milliliters are added from a wash bottle or capillary pipette. The neck of the flask above the mark is then dried with filter paper, the flask is stoppered and the contents are mixed thoroughly. It is a good practice to invert the flask from thirty to forty times, allowing the bubble to rise to the top each time.

Unfortunately such direct preparation of the standard solution is not always possible. In case of substances that cannot be obtained chemically pure—most alkalies, inorganic acids, and some salts—solutions of approximate content are prepared and these must subsequently be standardized. If in such a case one needs a solution that is as near as possible to some specified normality, it is best to prepare about 1.2 liters of a slightly more concentrated solution. After the titer of this has been found, the quantity of water which must be added to exactly one liter of the solution to bring it to the desired normality is easily calculated. The contraction inherent in mixing may be neglected. It is desirable in any case to check the titer of the solution after diluting.

It is possible to keep on hand concentrated stock solutions, like constant-boiling hydrochloric acid or strong sodium hydroxide, of exactly established concentration. The weight that must be diluted to one liter in order to obtain a solution of given normality is then known. In keeping stock solutions, water often evaporates and recondenses in droplets on the walls of the vessel; under such conditions it is, of course, necessary to "shake before using."

2. Standardization; Titer for Use and Corrected Titer.—If during the standardization the temperature deviates appreciably from the normal temperature, it is advisable to take this into account in order that the necessary corrections may be applied during subsequent use.

In general, the standardization of a solution requires a higher degree of accuracy than any other volumetric determination. An error in standardization recurs in all of the analyses that are made with the solution and under certain circumstances may enlarge the usual errors.

For ordinary purposes of volumetric analysis an accuracy of 0.1% in the standardization will suffice. If special investigations, such as the testing of standard substances, demand an appreciably higher accuracy, the entire experimental technique must be refined accordingly (see, for example, pp. 10, 17).

An average limit of error within 0.1% is not at all easy to obtain in the standardization. The following conditions must first be fulfilled:

(*a*) A suitable primary standard must be available (for details see p. 36).

(*b*) The weight of the standard substance used must not be too small. Two weighings are involved in every determination. If the error of an ordinary analytical weighing is taken as 0.1 mg., then for every standardization at least 200 mg. of standard substance must be taken if the weighing error is not to exceed 0.1%.

Potassium iodate as a primary standard has the disadvantage of a small equivalent weight (35.67). Only about 0.14 g. would have to be weighed out to secure a titration of 40 ml. in the standardization of a 0.1 N sodium thiosulfate solution. In such a case it is more advantageous to work with a solution of exactly known content. To prepare a liter of 0.1 N potassium iodate, 3.567 g. are used. An error of 0.2 mg. in weighing then corresponds to a relative error of about 0.6 part per 10,000 (0.006%) and hence need not be considered. The allowable error of a liter volumetric flask (according to National Bureau of Standards Circular C434) is 0.3 ml., corresponding to

0.03%, while that of a 50 ml. pipette amounts to 0.1%. In order that the error involved in the standardization be less than 0.1%, the glassware used must be calibrated more exactly than is required by these specifications. The weighing error can be reduced to a minimum and the flask and pipette error can be eliminated by dissolving a larger amount of standard substance in a known weight of water and weighing out portions of this solution.

In standardizing very dilute solutions (0.025 N or weaker) an accuracy of 0.1% cannot be obtained with direct weighing of the standard even if the latter has a fairly high equivalent weight. Here also a known solution of the substance should be prepared, and an aliquot part used for the standardization. A more dilute solution may be prepared by appropriate dilution of a stronger one, but it is then desirable to determine the *titer for use* (see p. 35) by careful standardization.

(*c*) The number of milliliters used in the standardization should not be too small lest the result be too greatly affected by the errors of reading and draining. If every reading is subject to an error of 0.01 ml. and there is an additional drainage error of 0.02 ml., then the error that is possible in every determination amounts to 0.04 ml. If 40 ml. is used this corresponds to an accuracy of 0.1%. Because of the drop error (see Volume I, p. 143) the possible total error is still greater.

(*d*) The titration should be made directly to the end-point. A back-titration with another standardized solution increases the possibility of error. Thus, for example, it is not advisable under ordinary circumstances, when standardizing hydrochloric acid against sodium carbonate as a primary standard, to add a slight excess of acid, boil out the carbon dioxide and determine the excess of acid with alkali that has been standardized using phenolphthalein.

(*e*) The reaction must proceed in only one direction during the standardization; disturbing side reactions cannot be tolerated.

(*f*) The standardization of a solution against another standardized liquid is to be avoided as far as possible, since the errors of the individual standardizations are combined in the final result. Nevertheless it is desirable to test independently standardized solutions against each other, as, for example, 0.1 N hydrochloric acid against 0.1 N alkali.

Every standardization, as well as every analysis, should be based on several parallel determinations. The greater the number of titrations that are made, the more completely are the observational errors canceled; the results are grouped around the true value according to the laws of probability.[1] If the titration error is disregarded, the arithmetical mean corresponds best to the true value.

The deviations of individual values from the mean are the individual errors, usually designated by d.

The individual error is of less importance than the precision with which the mean is determined. One way of expressing this mathematically is as the root mean square error of the mean

$$D_M \quad \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

Here Σd^2 is the sum of the squares of individual deviations from the mean and n is the number of determinations.

Suppose that the weight of primary standard taken is such that it requires 40 ml. of 0.1 N standard solution. If in three determinations the volumes 39.98, 39.97, and 40.04 ml. are consumed, the mean is 40.00 and

$$D_M \quad \sqrt{\frac{0.02^2 + 0.03^2 + 0.04^2}{3 \times 2}} = 0.022 \text{ ml.}$$

This mean square error corresponds to a precision of 0.055% in the result.

If in six determinations the volumes taken are 39.98, 39.97, 40.00, 40.02, 40.02, and 40.03 ml., the mean is again 40.00, but D_M is smaller

$$D_M = \sqrt{\frac{30 \times 10^{-4}}{6 \times 5}} \quad 0.01 \text{ ml.}$$

corresponding to a precision of 0.025%.

The smaller d and the greater n, the more exact is the result. However, since the accidental error decreases, not as the number of measurements but only as the square root of the number, a point is soon reached at which the extra precision attained by making more measurements does not justify the additional labor involved.

According to the rule generally used, the titer is expressed numerically in such a way that the decimal position before the last is certain, but the last one includes the uncertainty of the result. The titer of an approximately 0.1 N solution is given at most to four decimal places, and the last is uncertain by ±1. Ordinarily not the *absolute titer* but the *working titer*,[2] which differs relatively little from the former, is found by standardizing in the manner previously described. The *corrected titer* lies between these two values. As has already been mentioned in Volume I, an indicator usually changes a little before or after the equivalence-point rather than exactly at this point. Moreover, it is commonly necessary to add a drop in excess before the color change is perceptible to the eye.[3]

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[1] Discussions of errors in measurements and the theory of errors are given by: A. E. Korvezee and N. H. J. M. Voogd, *Chem. Weekblad*, **25**, 242 (1928); A. A. Benedetti-Pichler, *Ind. Eng. Chem., Anal. Ed.*, **8**, 373 (1936); I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 2nd ed., Macmillan, New York 1943, pp. 263–298; R. S. Livingston, *Physico Chemical Experiments*, Macmillan, New York 1939, pp. 10–19; T. B. Crumpler and J. H. Yoe, *Chemical Computations and Errors*, Wiley, New York 1940.

In many cases one can experimentally determine the excess (or deficiency) that is necessary for the change of the indicator and the drop error, and from this calculate the corrected titer. In standardizations of the highest precision a solution of the standard substance can be added from a weight burette until a few drops from the end-point. The titration is completed by adding a very dilute solution of the standard substance from an ordinary or microburette. In this way the drop error is practically eliminated.

3. Rational Equivalent Weight.—Atomic weights reported by the Committee on Atomic Weights of the International Union of Chemistry,[4] and the equivalent weights which are derived from them, refer to weighings in vacuo. Schoorl[5] has pointed out that it is not strictly appropriate to base practical analyses on these units, since one generally weighs in air and neglects the loss in weight due to air buoyancy. Under certain conditions this may give rise to an error of about 0.1%, which could easily be avoided. If the specific gravities of the substance weighed and of the weights (8.4 for brass) are known, the difference between the "international equivalent weight" and the "rational equivalent weight," which is valid for normal weighings in air, may be calculated. For this purpose the normal weight of a milliliter of air is taken as 1.205 mg.

Illustrations: According to the International Table for 1941[4] the equivalent weight of borax ($Na_2B_4O_7 \cdot 10H_2O$) as a standard for acidimetry is

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[2] *Cf.* J. Mika, *Z. anal. Chem.*, **96**, 401 (1934).

[3] N. Bjerrum, *Die Theorie der alkalimetrischen und acidimetrischen Titrierungen*, Enke, Stuttgart 1914, p. 74. See also Vol. I, p. 143.

[4] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, Eleventh Report, *J. Am. Chem. Soc.*, **63**, 845 (1941).

[5] N. Schoorl, *Z. anal. Chem.*, **57**, 209 (1918); *Chem. Weekblad*, **15**, 547 (1918). K. O. Schmitt, *Z. anal. Chem.*, **70**, 230 (1927). G. Bruhns, *Z. angew. Chem.*, **42**, 645 (1929). A. Thiele, *Chem.-Ztg.*, **53**, 813 (1929). N. Schoorl, *ibid.*, **54**, 133 (1930).

190.717. Using the value for the specific gravity of borax as 1.72, the rational equivalent weight becomes 190.607, or 0.06% less than the international value.

Since it is rather tedious to calculate the rational weight for each substance, Schoorl went a step further and proposed that *rational atomic weights*, referred to weighings in air, should be used in place of the international weights. By carrying through numerous calculations, he established that the specific volume of each element is fairly constant in its various compounds; then by using the calculated specific volumes and the international atomic weights he set up a table of rational atomic weights.

These rational weights would appear to deserve wider adoption in analytical practice. By their use one can readily exclude an error that is consciously committed through the use of international weights. For most purposes the list of rational weights given in the Appendix of this volume will suffice. Only in the most accurate analysis, such as in the testing of primary standards, would it be worthwhile to calculate the normal weight in air from the specific gravity and the international equivalent weight.

In the following chapters both the international and the rational equivalent weights are given.

4. Primary and Secondary Standards.—Some general observations on the use of primary standard substances are given in Vol. I (p. 12); it is of considerable importance to have such reference standards available because the accuracy of a volumetric analysis depends primarily upon the reliability of the standard used. Unfortunately there is not yet agreement in the literature concerning the requirements that should be met by a primary standard.

Wagner, who has rendered good service in the treatment of many titrimetric questions, has warned sharply[6] that it is more necessary to establish general rules for the testing of standard substances than to recommend new ones. He proposed that a recognized procedure be developed for the purification of a series of standards for *the same analytical purpose*. On the contrary, Kühling[7] suggested that of the available substances only a few should be selected and designated as "official standards." Sörensen aligned himself with this viewpoint in an important paper[8] on the question of uniform standard materials. Because of the significance of his observations, they are repeated in some detail below.

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[6] J. Wagner, *Dissertation*, Leipzig, 1898; the above is quoted from Sörensen.[8]

[7] O. Kühling, *Proceedings of the Fifth International Congress for Applied Chemistry*, *I*, Berlin 1903, p. 325.

[8] S. P. L. Sörensen, *Z. anal. Chem.*, **44**, 141 (1905). See also R. S. McBride, *J. Am. Chem. Soc.*, **34**, 394 (1912); F. D. Dodge, *Ind. Eng. Chem.*, **7**, 29 (1915).

With every standard substance there are associated sources of error of varying nature and magnitude, which may be recognized through larger or smaller deviations in the results obtained. According to Sörensen an ideal standard should be easy to prepare and to keep without change, testing of its purity should be simple, no complications should arise in handling it, and it should give results that are as nearly exact as possible. Discussing the selection of a substance, especially as to purity and applicability, Wagner stated:[9]

> "If it is necessary to test the purity of a preparation, after the usefulness of the compound itself has been established, it is perhaps satisfactory to dissolve part of the material and reprecipitate or recrystallize, then to compare the purified and original preparations in standardizations. If identical results are obtained the material was pure (or was unchanged by the treatment!). A test of this kind should also be made on the so-called guaranteed pure substances; in choosing a standard one should make sure that such a test can easily be performed. This simple test is only a preliminary step in determining whether a substance is generally suitable for standardizing. Comparison with another compound which acts similarly is also necessary; for example, iodates are compared with bromates, various acids with each other, and so on. This test is not conclusive, however, for one can see that chromate on the one hand and iodate or bromate on the other behave differently and the simple comparison does not show where the correct value lies. Therefore in doubtful cases, and for each volumetric group, at least one further comparison is necessary, using a standard substance which can be tested in two different ways. For instance, potassium tetraoxalate[10] may be determined alkalimetrically or oxidimetrically, and potassium acid iodate alkalimetrically or iodometrically."
>
> At the conclusion of his address before the Fifth International Congress (1903), Wagner adduced the principle that "the purity or strength of a substance to be used in standardizing should be established by comparison with two other compounds. It is not necessary that this be done in the same kind of reaction. Thus potassium acid iodate might be compared alkalimetrically with tetraoxalate, iodometrically with bromate."

Sörensen justly observed that this procedure does not decide conclusively whether a standard substance gives correct results or not, but rather whether it gives results that are just as correct—*or just*

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[9] J. Wagner, *Verhandl. Vers. Deutsch. Naturforscher u. Ärzte, Abt. angew. Chem., Agr.*, p. 183 (1901), quoted from Sörensen, *loc. cit.*

[10] **This compound, however, is not entirely suitable as a standard.**

as incorrect—as those obtained with the comparison material. If the two standards are impure to the same extent they show the same —though still incorrect—strength. On the other hand, Wagner's method will give correct information if the reference standard is ideally pure and if the methodic and specific errors are excluded as far as possible.

In any case, it is desirable to have primary standards which can easily be tested for purity. According to Sörensen it must be required of a really satisfactory standard substance that by simple qualitative tests (of known sensitivity) impurities may be shown to be absent of present in such small amount that the error caused thereby is not more than about 0.3 part per thousand. Therefore the qualitative tests for purity have more significance than any quantitative determination of the active strength of a standard, for ordinarily these quantitative determinations are subject to analytical errors of 0.1% or more.

In evaluating the results of qualitative tests it must be considered that not every impurity decreases the strength of the standard in proportion to the amount present. Rather one should distinguish between:

(*a*) *Inactive impurities*, which to their full extent diminish the effective titer of the substance, and

(*b*) *Active impurities*, which are consumed during the standardization and therefore affect the strength less than do the inactive ones. According to the circumstances they may raise or lower the effective strength.

For example, if a sodium chloride preparation contains 0.1% sodium sulfate, the effective strength as an argentometric standard is reduced to 99.9%. Potassium chloride would have a smaller effect; 100 parts of it correspond argentometrically to 78.4 parts of sodium chloride, therefore 0.1% of potassium chloride in sodium chloride decreases the effective strength by only about 0.022%. On the other hand, the presence of 0.1% sodium chloride in primary standard potassium chloride would *raise* the effective strength by 0.028%.

If a primary standard is used in different branches of volumetric analysis, a single impurity may be "active" in one reaction and "inactive" in another. As an illustration, sodium oxalate may be contaminated with the acid oxalate, bicarbonate or carbonate. In standardizing an acid against this salt, all of the impurities are active; for each 0.1% present, sodium carbonate increases the effective strength by 0.021%, sodium bicarbonate decreases it 0.025%, and sodium acid oxalate lowers it about 0.067%. However, if the oxalate is used for standardizing permanganate, the carbonate and bicarbonate behave as inactive impurities. Sodium acid oxalate is active but the effect is small; 0.1% increases the strength by 0.016%. This variability of active and inactive impurities should be considered in setting up purity requirements for primary standards.

Schoorl[11] specifies that the sum of all the impurities shall not exceed 0.01%. To be sure, one must allow for the effect of any active impurities if the requirement is intended to mean that the active strength shall correspond to at least 99.99% of the formula weight.

Schoorl recommends further that the physical homogeneity of the substance be tested. The refractive index of the crystals may be determined microscopically; at the same time the presence of dust or filter paper fibers may be detected. Better suited for the recognition of the latter impurities is an enrichment method ("solution test"). One prepares a concentrated aqueous solution in which the foreign particles may be seen, perhaps after long standing or centrifuging if their amount is small. On the other hand a microscopic examination offers also the possibility of detecting internal holes (vacuoles) in the crystals, which may be filled with air or more objectionably with mother liquor from the crystallization.

In many cases the qualitative testing is very simple. Pure sodium chloride upon being dissolved in water free from carbonic acid does not alter the p_H perceptibly, even after boiling and cooling in a carbon dioxide-free atmosphere. If the p_H of a 10% solution lies between 5 and 7, an impurity of more than 0.0005% of either hydrochloric acid or sodium carbonate is ruled out. These limits are indeed very narrow; they may be broadened by diluting the solution or by titrating with alkali to phenolphthalein or with acid to methyl yellow instead of determining the p_H.

With salts of strong bases and weak acids, or of weak bases and strong acids, the hydrolysis has to be taken into account in testing for acid or basic impurities. According to Sörensen, acid or basic salts are unsatisfactory as primary standards because there is no way of establishing the correct ratio of acid and basic components except by a quantitative determination. His opinion has been amply justified by experience. Thus the late Professor Schoorl (private communication) found that acid salts containing an excess of acid cannot in general be purified by recrystallization. It is not possible to remove an impurity of phosphoric acid by recrystallizing monosodium dihydrogen phosphate, though conditions are more favorable for purification of the potassium salt. No general rule can yet be given.

The testing of standard substances for a slight moisture content has great practical significance.[12] Water enclosed in the crystals is not driven out at 100°C. Sörensen,[8] for example, performed an experiment in which 5–6 g. of anhydrous sodium chloride was weighed accurately in a tube, dissolved in water and evaporated to dryness in an electric oven. After different periods and temperatures of drying the residue was weighed, with the following results:

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[11] N. Schoorl, *Chem. Weekblad*, **25**, 73, 534 (1928).

[12] *Cf.* T. W. Richards, *Z. physik. Chem.*, **46**, 189 (1903).

Drying Period, hours	Temperature, °C.	Water Remaining, %
4	180–250	0.19
12	180–250	0.14
12	295–300	0.09
12	295–300	0.07

Finally after 12 hours at about 380° the weight remained constant. Schoorl also studied the drying of moist sodium chloride (private communication). He found a water content of 0.37% at 120° and 0.06% at 360°.

Fortunately it is possible, according to Sörensen, to detect very small amounts of water qualitatively in substances which do not themselves decompose with the formation of water upon ignition, that is, in sodium chloride, oxalate, or carbonate, potassium bromate, etc. If a suitable sample is placed in a long test tube which has previously been heated and cooled in dry air, and the bottom of the tube is then heated to redness, even slight traces of water (far smaller than is ordinarily assumed) may be recognized as a film in the upper part of the tube. The sensitivity of this procedure should be tested for each particular material. Sörensen found 0.1% moisture in sodium oxalate after drying at 125°C.; in the qualitative test abundant condensation was noted. After further drying at 180–200° there still was 0.033% of water present which could be recognized easily by dew formation. With longer drying at 200–210° there remained 0.02% moisture which yielded a slight film in the qualitative test. After continued heating at 290° the water content dropped below 0.01% and the test became negative.

Sörensen concluded that a substance should be considered unsatisfactory as a primary standard if (*a*) it contains water of crystallization so that the water content cannot be controlled more exactly than by ordinary analytical methods, or (*b*) its chemical nature is such that water forms upon thermal decomposition, as is the case with acids, acid salts, and most organic compounds.

In the opinion of the authors, it is somewhat unreasonable to exclude substances containing water of crystallization, and others, like benzoic acid, as primary standards only because traces of adsorbed or occluded water, or slight efflorescence losses, cannot be detected qualitatively or quantitatively. Schoorl's studies on the preparation and use of pure oxalic acid dihydrate have shown this compound to be a valuable standard. After recrystallization the coarse crystals contain 0.2–0.3% of vacuole water. Schoorl grinds the crystals to less than 0.1 mm., dries them over phosphorus pentoxide and rehydrates over saturated sodium bromide solution. The surface condensation then amounts to about 0.01%. According to Schoorl[11] this method is of general use. If one allows a hydrate to effloresce in the presence of a suitable desiccant, the crystals crumble to a very fine powder and the occluded water is liberated. Then upon placing the dry powder in a system with a sufficiently high aqueous tension, the hydrate is regenerated without again forming vacuoles. Borax, $Na_2B_4O_7 \cdot 10H_2O$, is an example of a standard which can be treated in this way.

In all cases the conditions under which a proposed standard substance can be prepared chemically pure should be thoroughly investigated. In spite of the difficulty caused by adsorbed or occluded water, it is possible to establish conditions under which these impurities are kept as low as possible. Thus the enclosed water (mother liquor) may be removed as described above, or less completely by powdering the crystals and drying directly to the desired state (*cf.* Richards[12]). Finally the effective strength of the purified compound should be compared with that of an ideal substance conforming to Sörensen's requirements. In this comparison the total errors, including also the titration error, must amount to less than 0.3 part per thousand, this demanding refined experimental conditions. Nevertheless, when it has once been determined that a substance can be obtained sufficiently pure by a given process, there is no longer any reason for excluding it as a volumetric standard.

On the other hand, one should not be satisfied with merely testing the effective strength of the repeatedly recrystallized and dried compound against that of another arbitrary standard, as Wagner proposed. The comparison should be made with a primary standard of guaranteed purity and the determinations should be carried out with the highest accuracy.

It is of great value if the suitability of a primary standard can be tested through several possible reactions; errors caused by disturbing side reactions in a particular procedure may thus be detected. If a comparison is undertaken in one direction only, the reaction chosen should be one that is free from such disturbances. In general, neutralization and complex-formation processes meet this requirement. In oxidation-reduction titrations there are possibilities of induced reactions, while in precipitations there may be errors caused by adsorption or occlusion. It might then happen that an impure substance would appear to be pure through compensation of errors, or that doubt would unjustly be cast on the purity of a compound. For example, in testing oxalic acid with exactly standardized permanganate the results obtained are variable depending on the experimental conditions. Therefore in this case an alkalimetric titration is preferable for proving the applicability of the substance as a standard. This question will be considered in more detail later (Vol. III).

If the purity of an ideal standard can be proved by means of qualitative tests, these tests have to be repeated with each new lot of the material. On the other hand, the test for utility by means of exactly performed titrations does not have to be repeated each time if it has once been established for a similar lot. Of course, if the qualitative tests fail to give an absolute decision as to purity, the utility test cannot be avoided even with material especially purchased. However, if the standard is prepared according to a well-tried procedure, one may be spared the working test after each new preparation of the substance.

The most nearly ideal standard would appear to be one that satisfies Sörensen's requirements and is applicable in several branches of volumetric analysis. Such substances have been sought in vain many times, and there is still no "universal primary standard." Some compounds, like mercuric oxide, are perhaps capable of application in many ways, but with the sacrifice of ideal qualities in the endeavor to attain universality. These considerations will be taken up more specifically in Chapter III.

Potassium iodate is an excellent primary substance which can be used directly for the standardization of thiosulfate and of acids. If one reduces the iodate solution with pure sulfurous acid solution and boils out the excess of sulfur dioxide, the resulting known amount of iodide may be used in standardizing permanganate (potentiometrically or by Lang's method in the presence of cyanide) or silver nitrate (potentiometrically or by Fajan's method with an adsorption indicator). Potassium iodate therefore comes close to being a universal primary standard.

Sodium oxalate can serve as a standard for either acids or permanganate, and thus may be considered superior to sodium carbonate.

The more important of the foregoing considerations may be summed up in a few rules. First come those enunciated by Sörensen:

(*a*) *The purity of a primary standard substance should be tested by well-defined qualitative procedures whose sensitivity may be determined for each substance. Each new lot of the substance must obviously be subjected to these tests.*

(*b*) *If a substance whose purity has been established according to (a) is proposed as a primary standard, it must be tested further by various methods suited to the nature of the substance. This testing must be done as accurately as possible, but need be carried out only once.*

To these rules may be added several others. There are many compounds practically suited for standardizing except that satisfactory qualitative tests of their purity are lacking. If for each substance a procedure can be laid down once and for all by which it may be prepared entirely pure, there is no need of performing the tests for utility each time a new lot is made. However, if the substances are purchased on the market the utility tests must be carried out, each with a high degree of accuracy.

(*c*) *Primary standards or working standards must be capable of maintaining their composition unchanged during storage.*

(*d*) *The substances must not be so hygroscopic that they take up water during weighing.*

In this respect, for example, sodium carbonate is not entirely suitable for exact analyses because even on weighing in a glass-stoppered bottle it takes up traces of water.

In practice, primary standards of high equivalent weight deserve preference so that the error of weighing shall be inconsequential, especially in standardizing solutions weaker than 0.1 N.

5. Practical Divisions of Volumetric Analysis.—Reactions ordinarily used in volumetric analysis[13] may be classified as follows:

(*a*) Ion combination reactions.
  (*i*) Acid-base reactions.
  (*ii*) Precipitation reactions.
  (*iii*) Complex-formation reactions.
(*b*) Oxidation-reduction reactions.

(A) ION COMBINATION METHODS

(*i*) ***Acid–Base Reactions:*** Here belong the true *neutralization reactions* in which an acid or base is determined by converting it into a neutral salt in a titration with base or acid. In principle they consist in the union of hydrogen and hydroxyl ions to form water, when one deals with an aqueous system.

To this group also belong *displacement titrations* in which the anion of a weak acid is displaced from its salt by a strong acid, or the cation of a weak base by a strong base.

Illustrations: Titrations of bound alkali in sodium carbonate or bicarbonate, borax and the like, with hydrochloric acid, and of acid bound to aluminum, zinc, alkaloids, etc., with alkali, are typical displacement methods. Likewise, but in a broader sense, hydrolytic precipitations or complex formations may be classified as acid-base reactions, for in them the hydrogen-ion concentration changes suddenly with the first excess of reagent. In general one may designate as acidimetry or alkalimetry any titration whose end-point is recognized by a change in hydrogen-ion concentration.

(*ii*) ***Precipitation Reactions:*** In precipitation methods the ion being determined is precipitated by an oppositely charged ion of the standard solution. Any kind of ion can be determined titrimetrically in this way, if under suitable conditions it forms a slightly soluble compound and if the end-point can be shown by an indicator or other means.

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[13] *Cf.* Vol. I, pp. 4–5.

Practically, it is convenient to subdivide the methods into smaller groups; *argentometry*, for example, includes all precipitation titrations in which silver nitrate serves as the standard solution. In this book the individual branches of volumetric analysis will thus be classified according to the standard solution employed.

(*iii*) ***Complex Formation and the Formation of Slightly Dissociated Compounds:*** In these reactions an ion of the titrating solution converts the ion being determined into either a complex ion or a slightly dissociated compound. The titration of cyanide with silver nitrate is an example of the former, and that of chloride with mercuric nitrate, of the latter. All neutralization reactions really belong in this group, but it is convenient to classify them separately since they are all based on the reaction between hydrogen and hydroxyl ions.

(B) OXIDATION-REDUCTION METHODS

Usually the term *oxidimetry* is applied to reactions involving permanganate. Strictly speaking, it also covers iodimetry, cerimetry, bromometry, titanometry and other kinds of oxidation-reduction methods which draw their names from the standard solutions employed. The nomenclature is not entirely systematic; a grouping based only on the individual standard solutions would be clearer.

In many cases no sharp classification is possible. In the determination of lead as lead chromate the primary reaction is one of precipitation, but since the equivalence-point is not easy to perceive one actually titrates either the precipitate or the excess of precipitant iodimetrically in order to find how much chromate has combined with the lead. Since the titration is therefore iodimetric, the determination falls within the scope of iodimetry. On the other hand, the principles of precipitation reactions must also be considered in evaluating the titration error. In general, methods involving several reactions will be discussed in the section that would be most appropriate for the actual titration concerned.

This applies also to the methods of organic chemistry. In Volume I it was pointed out that these methods usually involve molecular reactions. However, the actual volumetric process (generally back-titration of a standard solution which has been added in excess) is classified most conveniently according to the titration method employed.

6. General Notes on the Performance of Titrations.—The proper choice of lighting and background is of importance in observing the color change of an indicator. Bright diffused daylight is excellent, though direct sunlight is generally unsatisfactory. With the dim or yellow artificial light sources of the older types, color changes lose their distinctness. With good white artificial light, and especially with the newer fluorescent lamps, the same accuracy can be obtained as by daylight.

While changes from colorless to yellow or rose and vice versa are easily perceptible with an ordinary tungsten filament lamp, two-color changes in the yellow-orange region are not sharply perceptible and may be reported several drops late under this illumination. A "daylight lamp" with blue bulb, or a fluorescent lamp, is more to be recommended for such cases.

A white background such as a plate of milk glass or sheet of white paper usually aids in the judging of a color change. Titration in a white porcelain dish is often proposed, but a white base will accomplish the same purpose. The color change may be observed by either transmitted or reflected light. If it is not very sharp, one may make comparisons with a suitable reference solution in a vessel similar to that used for titration. This solution should have the same volume as the titrated liquid at the end-point and should also contain the same quantity of indicator. For precipitation analyses it is convenient to use a solution which has already been titrated and then brought back with a slight excess of the ion being determined; thus in a Mohr titration of chloride such a solution containing a slight excess of chloride is used for comparison. If there is doubt as to whether a slight color change has occurred, the burette is read and then another drop, or part thereof, of the standard solution is added.

When the end-point is recognized by the appearance of a white turbidity or opalescence, as in the titration of cyanide in alkaline medium with silver nitrate, it is best to work with a dark background (black paper).

In general a continued swirling or stirring of the liquid during titration is to be recommended. It is customary to control the burette stopcock with the left hand and swirl the liquid with the right. If the agitation is not sufficiently vigorous, perceptible errors may be caused by local excesses of standard solution, particularly in precipitations or in oxidations where secondary reactions can take place. Various precautions and measures for avoiding overtitration have been suggested.[14] One simple precaution consists in using a flask with a small pocket or cup at the side, in which some of the solution can be retained. When the end-point is overrun the flask is tilted so that this solution is washed into the main body of liquid, restoring it to a slightly under-titrated condition. The end-point may then be approached more gradually.

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[14] *Cf.* F. Schulz, *Chem.-Ztg.*, **33**, 1187 (1909); R. Orthner, *ibid.*, **44**, 282 (1920); O. Hackl, *Z. anal. Chem.*, **58**, 194 (1919).

Usually Erlenmeyer flasks (preferably with wide necks) are employed as titration vessels. In alkalimetry and acidimetry it is especially important that these be made of a good variety of chemically resistant glass such as Pyrex. The softer glasses yield alkali as well as silicate when water, acids, or particularly alkalies, are boiled in them. It should be required of glassware that 100 to 200 ml. of water boiled therein for half an hour and cooled under a soda-lime tube shall not react alkaline to phenolphthalein.

In a few cases, such as in difficult saponifications with alcoholic alkali, Pyrex glass is not entirely satisfactory because some boric acid may be leached from it. Special low-boron glasses are available for such cases, or nickel beakers may be employed. In general, the vessels to be used should be tested in blank experiments under conditions comparable with those to be met in the analyses.

Stock solutions of alkalies should be kept in vessels of good glass because otherwise the vessels are attacked with the liberation of silicate and aluminate. Under some conditions the solutions may show a turbidity of calcium silicate. The resistance of a poor glass surface may be improved by paraffining.

In oxidimetry it often becomes necessary to let a solution stand for some time with excess reagent in order for the reaction to reach completion. If the reagent is volatile like bromine or iodine, it is absolutely necessary to use a glass-stoppered vessel such as an Erlenmeyer flask or bottle with ground-in stopper, or a so-called "iodine flask" which is designed especially for this purpose. The latter differs from a glass-stoppered Erlenmeyer flask in that the neck above the stopper is flared to resemble a funnel. This is convenient for introducing a potassium iodide solution, for example, after a period of standing with excess bromine.

B. ACID-BASE REACTIONS

CHAPTER III

ACIDIMETRY AND ALKALIMETRY

1. Indicators.—Numerous indicators have been proposed for revealing the end-points in neutralization titrations. In the first volume of this book there was some discussion of the so-called *color indicators*, which when in the ionized state have colors (and constitutions) that are different from those of the undissociated forms. These organic compounds comprise the most important class of indicators; practical details concerning their use will be given in this and the two succeeding chapters.

Colored salts or complex compounds whose color depends upon the reaction of the liquid have been recommended as indicators in the literature. An ammoniacal copper solution, for example, is decolorized by acid,[1] while ferric thiocyanate is deep red in acid solution but decomposes to ferric hydroxide in alkalies; ferric acetate and ferric meconate behave similarly. Indicators of this sort have scarcely any advantages in exact analysis. The organic indicators include so many compounds which change color sharply within quite narrow limits of hydrogen-ion concentration that there is very little practical interest in the use of other indicators.

The same applies to *precipitation indicators* for neutralizations, where the end-point is shown by precipitation of a slightly soluble acid or base. The use of such indicators as zinc salts (precipitation of zinc hydroxide), salts of silver or aluminum, or of alkaloids, is very old and has been proposed anew by Jellinek and Krebs.[2] Since these indicators are seldom employed in volumetric analysis they will not be discussed further here except to note that a mixture of mercuric cyanide and silver nitrate becomes turbid above a p_H of 4.2 (see p. 207).

Naegeli[3] introduced some *turbidity indicators* which offer more promise. If the p_H does not change rapidly near the equivalence-point of a titration, one must try to stop at a certain titration exponent; the narrower the transition interval, the more precisely can this point be located. Now there are no ideal indicators which change suddenly from acid color to alkaline color at a given p_H value. However, it has been found that many higher organic acids and bases or their salts behave as reversible colloids (semicolloids) which have sharp *flocculation points* when titrated with hydrogen or hydroxyl ions. The precipitation is not governed primarily by the law of mass action; the substances are coagulated within a very narrow p_H range rather than being precipitated over a fairly wide interval.

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[1] *Cf.* L. Kieffer, *Ann.*, **93**, 386 (1855); E. Falières, *Compt. rend.*, **129**, 110

[2] K. Jellinek and P. Krebs, *Z. anorg. allgem. Chem.*, **130**, 263, (1923).

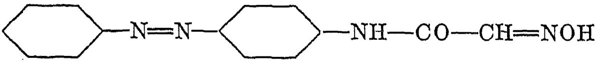
[3] C. Naegeli, *Kolloidchem. Beihefte*, **21**, 306 (1925).

If the salt of a very slightly soluble acid of high molecular weight is dissolved, then upon addition of a stronger acid the negatively charged anions are discharged by the hydrogen ions and the insoluble acid is suddenly flocculated. Similarly the salt of a high molecular weight base is coagulated by hydroxyl ions. Naturally all factors that affect the flocculation of colloids—such as the presence of salts, protective colloids or non-electrolytes like alcohol, the rate of addition of reagent, and the temperature—are of influence in determining at what point the turbidity occurs.[3]

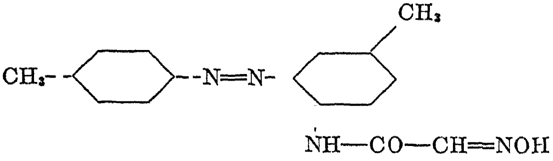
Naegeli sought especially for indicators capable of changing in quite strongly alkaline solutions, so that they might be used in titrations of very weak acids like boric acid or phenol which cannot be determined sharply with ordinary indicators. It would also be of interest to have turbidity indicators flocculating at various p_H values between 4 and 10. Such compounds might render the use of reference solutions unnecessary in many cases in which the end-points are ordinarily vague.

TURBIDITY INDICATORS ACCORDING TO NAEGELI AND TYABJI

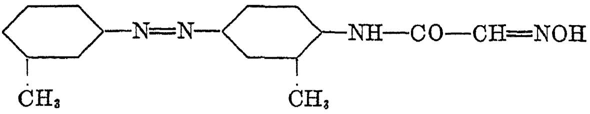
Indicator	Transition Region at 18°C p_H
I Isonitrosoacetyl-*p*-aminoazobenzene	10.7–11.0



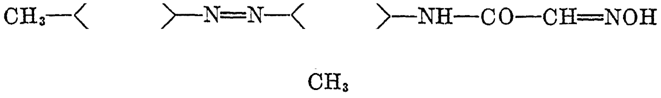
II. *p*-Tolueneazoisonitrosoacetyl-*p*-toluidine	11,55–11.



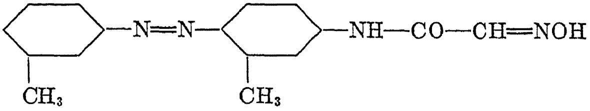
III. *m*-Tolueneazoisonitrosoacetyl-*o*-toluidine................ 9.3–9.4



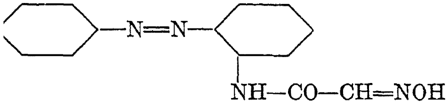
IV. *p*-Tolueneazoisonitrosoacetyl-*m*-toluidine................ 11.5–11.6



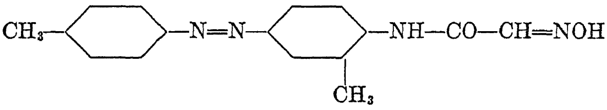
V. *m*-Tolueneazoisonitrosoacetyl-*m*-toluidine................ 11.1–11.5



VI. Isonitrosoacetyl-*o*-aminoazobenzene..................... 9.0–9.2



VII. *p*-Tolueneazoisonitrosoacetyl-*o*-toluidine................ 9.25–9.35



Several isonitrosoacetanilide derivatives were synthesized by Naegeli and Tyabji[4] and tested as turbidity indicators. In the accompanying table are listed the compounds which they found useful. The indicators are made up as 0.5 to 1% solutions of the sodium salts in alcohol (but these are not stable for very long), and 1 ml. is taken for 40 ml. of solution to be titrated. Turbidity generally appears near the lower p_H value shown for each compound, though this point varies with the conditions. Nevertheless, with a given solution the transition interval is not much greater than 0.1 p_H unit, as may be seen from the following ranges observed with indicator I:

Borax and sodium hydroxide........................	10.66–10.78
Phosphate and sodium hydroxide.....................	10.80–10.97
Glycine and sodium hydroxide.......................	10.91–10.9

With indicator I it is possible to make titrations of boric or arsenious acid. An excess of alkali must first be added and then the indicator, after which the solution is titrated back with standard acid. Indicator V is suggested for the titration of glycine as an acid. However, although small temperature variations need not be considered, the flocculation points are influenced by so many factors that analysts will probably prefer in general to use other methods of determining these compounds (see pp. 115, 160, 287).

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[4] C. Naegeli and A. Tyabji, *Helv. Chim. Acta,* **15,** 403, 758 (1932).

In highly colored liquids it may be impossible to perceive color changes. In such cases one can often make good use of a *fluorescence indicator*. Certain compounds when exposed to ultraviolet radiation emit visible light, and this property may disappear if the ionic state of the compound is changed. Thus the salts of some organic acids are capable of fluorescing while the free acids are not.

Robl[5] found that a 0.2% aqueous solution of umbelliferone is suitable as an indicator for the titration of strong or moderately strong acids with strong bases. About 10 drops are used per 20 ml. of liquid and the titration is made under radiation from a Hanovia ultraviolet lamp. While the solution is still acid it shows a pale blue light and a sky-blue fluorescence is noted as the alkali enters. This disappears on shaking until the end-point is reached, when it remains permanently. The indicator has a transition interval of from 6.5–7.6.

According to Kocsis and Nagy,[6] chromotropic acid is a useful fluorescence indicator with about the same transition interval as methyl orange. It shows no fluorescence in acid medium and a bright blue in alkaline.

2. Stock Solutions of Indicators.—The general properties of acid-base indicators were discussed in Volume I and the behavior of these compounds from the standpoint of organic chemistry has been amply covered in special texts on the subject, therefore only the more practical details will be presented here. Some of the older indicators like gallein and cochineal, which have no advantages, and hematoxylin, which even has disadvantages, are purposely omitted. In general one can get along well with the indicators listed in the accompanying table, all of which have proved to be satisfactory for practical use.

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[5] R. Robl, *Ber.*, B **59**, 1725 (1926); see also L. J. Descha, *J. Am. Chem. Soc.*, **42**, 1350 (1920), **48**, 1493 (1926). Several other indicators are discussed in *Acid-Base Indicators* by I. M. Kolthoff, translation by C. Rosenblum, Macmillan, New York 1937, pp. 177–180. See also K. A. Jensen, *Z. anal. Chem.*, **94**, 177 (1933), **117**, 50 (1939); E. Briner and E. Perrottet, *Helv. Chim. Acta*, **23**, 1253 (1940); E. A. Kocsis and E. Pettkó, *Z. anal. Chem.*, **124**, 45 (1942); E. A. Kocsis and G. Zádor, *ibid.*, **124**, 42, 274 (1942).

[6] E. A. Kocsis and Z. von S. Nagy, *ibid.*, **108**, 317 (1937).

ACID-BASE INDICATORS

Indicator	Approximate p_H Range
Tropeolin OO or thymol blue (acid range)	2–3
Methyl yellow, methyl orange or bromophenol blue	3–4
Methyl red or bromocresol green	4–6
Bromothymol blue	6–7
Phenol red or neutral red	7–8
Phenolphthalein or thymol blue (alkaline range)	8–9
Thymolphthalein	9–10
Alizarin yellow	10–11
Tropeolin O or nitramine	11–12
Trinitrobenzoic acid	12–13

Nevertheless, since in working with colored solutions or in titrating to a given exponent it is frequently convenient to have a greater selection of indicators available, directions for preparing several additional solutions will be included below.

Tropeolin OO (diphenylaminoazobenzene sodium sulfonate): Transition interval 1.3 (red) to 3.2 (yellow). Stock solution 0.1% in water, of which 1 or 2 drops are used per 10 ml. of solution to be titrated.

Thymol blue (thymolsulfonephthalein): Transition interval 1.2 (red) to 2.8 (yellow). Stock solution 0.1%, prepared by dissolving 100 mg. either in 20 ml. of warm alcohol or in 4.3 ml. of 0.05 N sodium hydroxide (by rubbing in a mortar), and diluting to 100 ml. with water. Use 1 to 3 drops per 10 ml. of solution.

Methyl yellow (dimethylaminoazobenzene): Transition interval 2.9 (red) to 4.0 (yellow). Stock solution 0.1% in 90% alcohol; 1 drop used per 10 ml. The color change from yellow to orange can be perceived somewhat more sharply than the change of methyl orange from orange to rose, so that methyl yellow seems to deserve preference in many cases.

Methyl orange (dimethylaminoazobenzenesulfonic acid): Transition interval 3.0 (red) to 4.4 (orange-yellow). Stock solution 0.1% or less in water; 1 drop used per 20 ml.

If during the titration there is formed a substance that is insoluble in water and it tends to remove methyl yellow from the aqueous phase, methyl orange is a more suitable indicator. This occurs, for example, in titrations of soaps with acid. The fatty acids formed extract methyl yellow so that the end-point cannot be perceived. Likewise methyl orange is more appropriate for titrations in the presence of immiscible organic solvents such as carbon tetrachloride or ether, as in the determination of alkaloids after extraction with a solvent. Iodoeosin has also been proposed as an indicator for such cases.[7]

Bromophenol blue (tetrabromophenolsulfonephthalein): Transition interval 3.0 (yellow) to 4.6 (violet-blue). Stock solution 0.1% in 20% alcohol (*cf.* thymol blue) or, as the sodium salt, in water. 100 mg. of the free acid requires 3.0 ml. of 0.05 N sodium hydroxide. From 1 to 3 drops of indicator are taken for 10 ml. of solution.

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[7] F. Mylius and F. Foerster, *Ber.*, **24**, 1482 (1891); *Z. anal. Chem.*, **31**, 240 (1892).

p-Ethoxy chrysoidine[8] (*p*-ethoxybenzeneazo-*m*-phenylenediamine): Transition interval 3.5 (red) to 5.5 (yellow). Stock solution 0.1% in 90% alcohol, or the hydrochloride may be dissolved in water; 1 drop is used per 25 ml.

Alizarin sodium sulfonate (dihydroxyanthraquinone sodium sulfonate): Transition interval 3.7 (yellow) to 5.2 (violet). Stock solution 0.1% in water; 1 to 3 drops for 10 ml. of solution.

Methyl red (dimethylaminoazobenzene-*o*-carboxylic acid): Transition interval 4.4 (red) to 6.2 (yellow). Stock solution 0.1% in 60% alcohol or, as the sodium salt, in water; 1 or 2 drops used per 10 ml.

Bromocresol green (tetrabromo-*m*-cresolsulfonephthalein): Transition interval 4.0 (yellow) to 5.6 (blue). Stock solution 0.1% in 20% alcohol or, as the sodium salt, in water; 1 to 3 drops used per 10 ml.

Benzoyl auramine G:[9] Transition interval 5.0 (violet) to 5.6 (pale yellow). Stock solution 0.25% in methanol; 1 or 2 drops used per 10 ml.

Since this compound is not stable in aqueous solution, hydrolyzing slowly in neutral medium, more rapidly in alkalies and still more rapidly in acids, the indicator should not be added until one is ready to titrate. The acid quinoid form of the compound is dichroic, showing a red-violet in thick layers and blue in thin. At a p_H of 5.4 the indicator appears a neutral gray color by daylight or a pale red under tungsten light. The change to yellow is easily recognized in either case.

p-Nitrophenol: Transition interval about 5 (colorless) to 7 (yellow). Stock solution 0.2% in water; 1 to 5 drops used per 10 ml.

Chlorophenol red (dichlorophenolsulfonephthalein): Transition interval 5.0 (yellow) to 6.6 (red). Stock solution 0.1% in 20% alcohol or, as the sodium salt, in water. 100 mg. of the free acid requires 4.8 ml. of 0.05 N sodium hydroxide. From 1 to 3 drops of indicator are needed for 10 ml. of solution.

Bromocresol purple (dibromo-*o*-cresolsulfonephthalein): Transition interval 5.2 (yellow) to 6.8 (purple). Stock solution 0.1% in 20% alcohol or, as the sodium salt, in water; 1 to 3 drops used per 10 ml.

Bromothymol blue (dibromothymolsulfonephthalein): Transition interval 6.0 (yellow) to 7.6 (blue). Stock solution 0.1% in 20% alcohol or, as the sodium salt, in water. 100 mg. of the free acid requires 3.2 ml. of 0.05 N sodium hydroxide. From 1 to 3 drops of indicator are taken for 10 ml. of solution.

Indo-oxine[10] (5,8-quinolinequinone-8-hydroxy-5-quinolyl-5-imide): Transition interval 6.0 (red) to 8.0 (blue). Stock solution 0.05% in alcohol, of which 0.2 ml. is used per 50 ml. of solution to be titrated.

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[8] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **115**, 185 (1939).

[9] J. T. Scanlan and J. D. Reid, *Ind. Eng. Chem., Anal. Ed.*, **7**, 125 (1935).

[10] R. Berg and E. Becker, *Z. anal. Chem.*, **119**, 81 (1940).

Phenol red (phenolsulfonephthalein): Transition interval 6.8 (yellow) to 8.0 (red). Stock solution 0.1% in 20% alcohol or, as the sodium salt, in water. 100 mg. of the free acid requires 5.7 ml. of 0.05 N sodium hydroxide. From 1 to 3 drops of indicator are needed for 10 ml. of solution.

Neutral red (dimethyldiaminophenazine chloride): Transition interval 6.8 (red) to 8.0 (yellow-orange). Stock solution, 100 mg. dissolved in 60 ml. of alcohol and diluted to 100 ml. with water; 1 or 2 drops are used per 10 ml.

Rosolic acid (corallinphthalein, principally): Transition interval 6.9 (red) to 8.0 (yellow). Stock solution 0.5 g. dissolved in 50 ml. of alcohol and diluted to 100 ml. with water; 1 to 3 drops are used per 10 ml. The indicator is especially suited for titrations of alcoholic solutions.

Cresol red (*o*-cresolsulfonephthalein): Transition interval 7.2 (yellow) to 8.8 (red). Stock solution 0.1% in 20% alcohol or, as the sodium salt, in water. 100 mg. of the free acid requires 5.3 ml. of 0.05 N sodium hydroxide. Add 1 to 3 drops of indicator to 10 ml. of solution.

Ethyl bis-(2,4-dinitrophenyl) acetate: Transition interval 7.4 (colorless) to 9.1 (deep blue). Stock solution prepared by saturating a solution containing equal volumes of ethanol and acetone with the indicator; 1 drop serves for 20 ml. of solution to be titrated.

The preparation of this compound is described by Fehnel and Amstutz[11] who recommend it for the titration of orange- and red-colored solutions or dark oils in which the end-point of phenolphthalein is not easily visible. The indicator is an orange solid which after crystallization from benzene gives pale yellow crystals melting at 150–153.5°C., uncorrected. It is commercially available.

α-Naphtholphthalein: Transition interval 7.3 (pale yellow-red) to 8.7 (green). Stock solution, 100 mg. dissolved in 50 ml. of alcohol and diluted to 100 ml. with water; from 1 to 3 drops are taken for 10 ml.

Phenolphthalein: Transition interval 8.2 (colorless) to 10.0 (red). Stock solution (*a*) 1%, prepared by dissolving 1 gram in 60 ml. of alcohol and diluting to 100 ml. with water; (*b*) 0.1%, prepared by diluting 10 ml. of (*a*) with 90 ml. of 50% alcohol. The latter should be used for titrations to a given exponent, otherwise either may be employed; 1 drop of (*a*) or 1 to 4 drops of (*b*) are taken for 10 ml. of solution.

Thymol blue (see p. 53): Transition interval in alkaline range 8.0 (yellow) to 9.6 (blue); 1 to 4 drops of 0.1% solution per 10 ml.

α-Naphtholbenzein: Transition interval 9.0 (colorless) to 11.0 (blue). Stock solution 0.1% in 70% alcohol; 1 to 4 drops per 10 ml.

Thymolphthalein: Transition interval 9.3 (colorless) to 10.5 (blue). Stock solution 0.1% in alcohol; 1 or 2 drops used per 10 ml.

Alizarin yellow (*p*-nitroanilineazo sodium salicylate): Transition interval

[11] E. A. Fehnel and E. D. Amstutz, *Ind. Eng. Chem., Anal. Ed.*, **16,** 53 (1944); *cf.* V. von Richter, *Ber.*, **21,** 2470 (1888).

10.1 (yellow) to 12.1 (violet). Stock solution 0.1% in water; 1 to 3 drops per 10 ml.

Tropeolin O (sodium salt of sulfanilic acid azoresorcinol): Transition interval 11.0 (yellow) to 13.0 (orange-brown). Stock solution 0.1% in water; 1 to 3 drops per 10 ml.

Nitramine (picrylmethylnitramine): Transition interval 10.8 (colorless) to 13.0 (red-brown). Stock solution 0.1%, prepared by dissolving 100 mg. in 60 ml. of alcohol and diluting to 100 ml. with water; 1 to 5 drops are used per 10 ml. The solution should be kept in the dark as nitramine is unstable; on boiling with alkali it decomposes quickly. Fresh solution should be prepared every few months.

Trinitrobenzoic acid: Transition interval 12.0 (colorless) to 13.4 (orange-red). Stock solution 0.1% in water; 1 or 2 drops are used per 10 ml. of solution.

Mixed Indicators: To obtain sharper color changes it is appropriate in many cases to use mixtures of indicators such as those which change at about the desired p_H and have contrasting colors at that point. Especially in titrating to a given titration exponent are such mixtures advantageous.

For example, a mixture of equal parts of bromocresol purple and bromothymol blue has been recommended by Cohen.[12] This indicator is yellow-green at p_H 6.0 and pure blue at 6.8, showing a sharp change. Cohen also used mixtures of bromophenol blue with either cresol red or bromocresol purple. Simpson[12] suggested a mixture of six parts of thymol blue with one part of cresol red (see p. 133).

An indicator may also be mixed with an indifferent dye in order to make the change more distinct. Thus the rather difficultly recognizable change of methyl orange by artificial light is improved considerably when indigo carmine is added. Such measures were proposed long ago by Luther.[13] Moerk[14] systematically tested various mixtures for the most favorable proportions and recommended an aqueous solution of 1 g. methyl orange and 2.5 g. indigo carmine per liter. It is best preserved in a brown bottle. The color is yellow-green in alkaline solution, becomes gray at a p_H of 4 and shifts toward violet with decreasing p_H. The change is easily visible even by artificial light and according to the author's experience the indicator is well suited for many titrations.

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[12] A. Cohen, *J. Am. Chem. Soc.*, **44**, 1851 (1922). See also J. L. Lizius, *Analyst*, **46**, 355 (1921); F. H. Carr, *ibid.*, **47**, 196 (1922); G. Chabot, *Bull. soc. chim. Belg.*, **34**, 202 (1925); S. G. Simpson, *Ind. Eng. Chem.*, **16**, 709 (1924).

[13] R. Luther, *Chem.-Ztg.*, **31**, 1172 (1907); *cf.* C. Kirschnik, *ibid.*, **31**, 960 (1907); M. Scholtz, *Z. Elektrochem.*, **10**, 549 (1904).

[14] F. X. Moerk, *Am. J. Pharm.*, **93**, 675 (1921).

Hickman and Linstead[15] suggested a solution of 1 g. methyl orange and 1.4 g. xylene cyanole FF in 500 ml. of 50% alcohol. This is green in alkaline solution, neutral gray at a p_H of 3.8–4, and red in acids. It has been quite widely used.

Using the same principle, the color change of phenolphthalein can be improved by addition of a dye that is complementary to red. For determining the acidity of milk an alcoholic solution containing 0.1% phenolphthalein and 0.2% methyl green is well adapted. To 10 ml. of milk one adds 1 or 2 drops of indicator. The color is green at a p_H of 8.0, gray at 8.4, grayish blue at 8.8 and suddenly a beautiful violet at 9.0. Because methyl green is unstable to light, the stock solution should be kept in a dark bottle.

Mixed indicators are especially useful in cases where the p_H curve has only a small slope at the equivalence-point, since they show their color change in a small and definite p_H interval. Using a mixture which changes just at the equivalence-point one can titrate without a reference solution. In view of the consequent practical importance of suitable mixtures, a number of them are listed in the accompanying table. Most of these were tested by the author; the methyl orange-bromocresol green mixture with p_T of 4.3 was introduced by Pierre, Tully and Ashburn[16] for use in the analysis of phosphate fertilizers. In the table, the column headed p_T gives the p_H at which the mixtures change their colors sharply.

Among weak acids and bases which may be titrated advantageously with the aid of mixed indicators are *pyridine* (methyl yellow–methylene blue, $p_T = 3.7$ with 0.1 N solutions) and *phosphoric acid* as a dibasic acid (α-naphtholphthalein–phenolphthalein, $p_T = 9.7$). *Acetic acid* may be neutralized with ammonia to a p_T of 7.0 without a reference solution if a neutral red–methylene blue indicator is employed.

3. Titration Exponents, Water Color, Necessary Excess of Reagent.

—The particular p_H value which should be attained at the equivalence-point of a titration has been designated by Bjerrum[17] as the *titration exponent*, p_T. Noyes[18] has estimated that for two-colored indicators from 5 to 30% conversion into the opposite form is necessary to show a difference from the pure acid or pure alkaline color. Thus with methyl orange from 5 to 20% of the yellow form must be converted to red in order to show a change from yellow, whereas from 20 to 30% of the red form must have gone over to yellow before

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[15] K. C. D. Hickman and R. P. Linstead, *J. Chem. Soc.*, **121**, 2502 (1922).

[16] W. H. Pierre, N. Tully, and H. V. Ashburn, *Ind. Eng. Chem., Anal. Ed.*, **10**, 72 (1938).

[17] N. Bjerrum, *Die Theorie der alkalimetrischen and acidimetrischen Titrierungen*, Enke, Stuttgart 1914.

[18] A. A. Noyes, *J. Am. Chem. Soc.*, **32**, 827 (1910).

SUMMARY OF MIXED INDICATORS

Composition of Indicator Solution	p_T	Acid Color	Alkaline Color	Notes
1 part 0.1% methyl yellow in alcohol 1 part 0.1% methylene blue in alcohol *Keep in a dark bottle*	3.25	Blue-violet	Green	Still green at p_H 3.4, blue violet at 3.2; excellent indicator
1 part 0.1% hexamethoxytriphenylcarbinol in alcohol 1 part 0.1% methyl green in alcohol *Keep in a dark bottle*	4.0	Violet	Green	Color is blue violet at p_H 4.0
1 part 0.1% methyl orange in water 1 part 0.25% indigo carmine in water *Keep in a dark bottle*	4.1	Violet	Green	Good indicator, especially in artificial light
1 part 0.1% methyl orange in water 1 part 0.1% aniline blue in water	4.3	Violet	Green	
1 part 0.1% bromocresol green sodium salt in water 1 part 0.02% methyl orange in water	4.3	Orange	Blue-green	Yellow at p_H 3.5, greenish yellow at 4.05, weakly green at 4.3
3 parts 0.1% bromocresol green in alcohol 1 part 0.2% methyl red in alcohol	5.1	Wine-red	Green	Very sharp color change; excellent indicator
1 part 0.2% methyl red in alcohol 1 part 0.1% methylene blue in alcohol *Keep in a dark bottle*	5.4	Red-violet	Green	Color is red-violet at p_H 5.2, a dirty blue at 5.4, and a dirty green at 5.6
1 part 0.1% chlorophenol red sodium salt in water 1 part 0.1% aniline blue in water	5.8	Green	Violet	Pale violet at p_H 5.8
1 part 0.1% bromocresol green sodium salt in water 1 part 0.1% chlorophenol red sodium salt in water	6.1	Yellow-green	Blue-violet	Blue-green at p_H 5.4, blue at 5.8, blue with a touch of violet at 6.0, blue-violet at 6.2
1 part 0.1% bromocresol purple sodium salt in water 1 part 0.1% bromothymol blue sodium salt in water	6.7	Yellow	Violet-blue	Yellow-violet at p_H 6.2, violet at 6.6, blue-violet at 6.8

SUMMARY OF MIXED INDICATORS—*Continued*

Composition of Indicator Solution	p_T	Acid Color	Alkaline Color	Notes
2 parts 0.1% bromothymol blue sodium salt in water 1 part 0.1% azolithmin in water	6.9	Violet	Blue	
1 part 0.1% neutral red in alcohol 1 part 0.1% methylene blue in alcohol *Keep in a dark bottle*	7.0	Violet-blue	Green	Violet-blue at p_H 7.0; excellent indicator
1 part 0.1% neutral red in alcohol 1 part 0.1% bromothymol blue in alcohol	7.2	Rose	Green	Dirty green at p_H 7.4, pale rose at 7.2, clear rose at 7.0
2 parts 0.1% cyanine in 50% alcohol 1 part 0.1% phenol red in 50% alcohol	7.3	Yellow	Violet	Orange at p_H 7.2, beautiful violet at 7.4; color fades on standing
1 part 0.1% bromothymol blue sodium salt in water 1 part 0.1% phenol red sodium salt in water	7.5	Yellow	Violet	Dirty green at p_H 7.2, pale violet at 7.4, strong violet at 7.6; excellent indicator
1 part 0.1% cresol red sodium salt in water 3 parts 0.1% thymol blue sodium salt in water	8.3	Yellow	Violet	Rose at p_H 8.2, distinctly violet at 8.4; excellent indicator
2 parts 0.1% α-naphtholphthalein in alcohol 1 part 0.1% cresol red in alcohol	8.3	Pale rose	Violet	Pale violet at p_H 8.2, strong violet at 8.4
1 part 0.1% α-naphtholphthalein in alcohol 3 parts 0.1% phenolphthalein in alcohol	8.9	Pale rose	Violet	Pale green at p_H 8.6, violet at 9.0
1 part 0.1% phenolphthalein in alcohol 2 parts 0.1% methyl green in alcohol *Keep in a dark bottle*	8.9	Green	Violet	Pale blue at p_H 8.8, violet at 9.0
1 part 0.1% thymol blue in 50% alcohol 3 parts 0.1% phenolphthalein in 50% alcohol	9.0	Yellow	Violet	From yellow through green to violet; excellent indicator

SUMMARY OF MIXED INDICATORS—*Continued*

Composition of Indicator Solution	p_T	Acid Color	Alkaline Color	Note
1 part 0.1% phenolphthalein in alcohol 1 part 0.1% thymolphthalein in alcohol	9.9	Colorless	Violet	Rose at p_H 9.6, violet at 10; change can be seen sharply
1 part 0.1% phenolphthalein in alcohol 2 parts 0.2% Nile blue in alcohol	10.0	Blue	Red	Violet at p_H 10; excellent indicator
2 parts 0.1% thymolphthalein in alcohol 1 part 0.1% alizarin yellow in alcohol	10.2	Yellow	Violet	Can be seen sharply
2 parts 0.2% Nile blue in water 1 part 0.1% alizarin yellow in alcohol	10.8	Green	Red-brown	

the difference from pure acid color is distinct. In other words, the color intensity of the acid form is greater than that of the alkaline. The author found with methyl yellow that 10% of the red form can be recognized in the presence of the yellow; in titrating to this color a p_T of 4.0 is reached.

The titration exponent which is attained when using a one-color indicator depends markedly upon the indicator concentration, as has been explained in Vol. I (p. 94). The color of the solution is determined by the concentration of the colored indicator ion. The latter, in accordance with the law of mass action, varies directly with the total indicator concentration and inversely with the hydrogen-ion concentration (for an acid indicator like phenolphthalein). If now two solutions are prepared, one of which contains ten times as much phenolphthalein as the other, and each is titrated with alkali to the same color, the stronger solution will show this color when its hydrogen-ion concentration is still ten times as great as that of the weaker, that is, when the p_H is one unit less. From this it is clear that one might titrate to a p_T of 8.2 using much indicator or to 9.2 using very little. With *p*-nitrophenol the p_T may be varied between 4 and 5.6 through suitable choice of concentrations. On the other hand, the p_T of thymolphthalein remains close to 10 because this indicator is only slightly soluble; after the saturation concentration is reached no further increase in color intensity takes place.

The accuracy with which one can attain a given titration exponent is quite good, but depends upon the nature of the indicator. It is best to employ an indicator having a small transition interval so that the color change may be observed sharply with relatively small differences in p_H. In general an accuracy of about 0.4 p_H unit may be expected though with special precautions such as the use of a reference solution one may come within 0.2 or even better. For exact work the reference solution must have a strictly defined p_H, equal to that of the titrated system at the equivalence-point, and also it must contain the same quantities of indicator and electrolyte in the same volume of solution. The titration is stopped when the two solutions have the same shade. For example, to determine the free acid in an ammonium acetate solution one uses phenol red or neutral red as indicator and a buffer mixture of p_H 7.0 as reference solution. This p_H corresponds to that of a pure ammonium acetate solution (see also p. 57).

Obviously it is not always necessary to reach a definite p_H. The change in p_H at the end-point is generally large enough so that the transition interval of a suitable indicator will be crossed upon the addition of but very little standard solution. This is the case for many indicators in the titration of strong acids with strong bases; the color change is sharp and there is no need for a reference solution. It is then immaterial whether the indicator changes in weakly acid solution or weakly alkaline, so long as the shift occurs between p_H limits of about 5 and 9.

However, if one works with an indicator whose transition range lies beyond these limits, it must be considered that in pure water or a neutral salt solution a perceptible amount of alkali or acid will be required to change the color of the indicator. Thus with methyl yellow or methyl orange (both of which are useful in alkalimetric titrations because of freedom from carbon dioxide interference) the color begins to change at a p_H of about 4. This corresponds to a hydrogen-ion concentration of 10^{-4} N, or to 0.1 ml. of 0.1 N acid per 100 ml. If one were titrating 50 ml. of 0.1 N strong base with acid, an *excess* of 0.2% of acid would be consumed before any change could be observed. The unpracticed eye judges this first change best by comparison with a solution of the indicator in pure water (*water color.*) When necessary, a correction (*indicator correction*) may be applied for the unavoidable excess. Such a correction naturally refers only to the cases where theoretically one does not have to titrate to a given p_T.

In titrating from the acid side to the alkaline, using methyl yellow as indicator and dealing with strong electrolytes, one titrates to the water color. The correction then is naturally smaller and it may ordinarily be neglected for practical purposes.

The accompanying table lists various indicators and the titration exponents for which they are appropriate at room temperature. For work at higher temperatures account should be taken of the fact that basic indicators become much less sensitive toward hydrogen ions (*cf.* Vol. I, p. 95), although acid indicators are affected very little. Methyl yellow and methyl orange, for example, are unsatisfactory for titrations with 0.1 N solutions at higher temperatures.

The table also indicates how many milliliters of 0.1 N hydrochloric

TITRATION EXPONENT AND NECESSARY EXCESS OF STRONG ACID OR BASE FOR VARIOUS INDICATORS

Indicator	p_T	Color at the Given p_T	Reference Color	Excess of 0.1 N Acid or Base at p_T, ml. per 100 ml.
Thymol blue	2.6	Orange	Yellow	2.5 (acid)
Tropeolin OO	2.8	Orange-yellow	Yellow	1.6
Methyl yellow	3.9	Orange-yellow	Yellow	0.12
Methyl orange	4.0	Orange	Orange-yellow	0.10
Bromophenol blue	4.0	Purple-green	Purple	0.10
Bromocresol green	4.4 acid	Yellow-green	Yellow (acid)	0.04
	5.4 alk.	Blue-green	Blue (alk.)	0.004
Methyl red	4.8 acid	Red	Red (acid)	0.016
	5.8 alk.	Orange	Yellow (alk.)	0.0016
Bromocresol purple	6.0	Purple-green	Purple (alk.)	—
Chlorophenol red	6.0	Rose	Red (alk.)	—
Bromothymol blue	6.4 acid	Yellow-green	Yellow (acid)	—
	7.4 alk.	Blue-green	Blue (alk.)	—
Phenol red	7.0 acid	Orange	Yellow (acid)	—
	7.8 alk.	Rose	Red (alk.)	—
Neutral red	7.0 acid	Rose	Red (acid)	—
	7.8 alk.	Orange	Orange-yellow (alk.)	—
Cresol red	7.4 acid	Orange	Yellow (acid)	—
	8.4 alk.	Red	Dark red (alk.)	—
Thymol blue	8.4 acid	Yellow-green	Yellow (acid)	—
	9.4 alk.	Blue-green	Blue (alk.)	0.016 (alk.)
Phenolphthalein				
1.0% solution	8.4	Rose	Colorless	—
0.1% solution	9.4	Rose	Colorless	0.016
Thymolphthalein	10.0	Pale blue	Colorless	0.06
α-Naphtholbenzein	10.0	Green	Colorless	0.06
Alizarin yellow	11.0	Lilac	Yellow	0.6
Nitramine	11.5	Orange-brown	Colorless	2.0

acid or sodium hydroxide are necessary to bring 100 ml. of pure water to the p_T that is given. This excess may be taken into account as a correction if the error is not eliminated by use of a reference solution. The table does not apply when one deals with a weak acid or a weak base.

Illustration: In the titration of 0.1 N sodium hydroxide with 0.1 N hydrochloric acid to a p_T of 4.0 using bromophenol blue, the necessary excess of acid corresponds to 0.1 ml. per 100 ml. of solution at the equivalence-point, or a titration error of 0.2%. On the other hand, if the solution consists of 0.1 N papaverine hydrochloride in which free acid is being titrated, the acid is neutralized at a p_T of 3.9–4.0 and no correction should be applied.

In the table are also given the water colors and the pure acid and alkaline colors of the indicators. With a compound like methyl red, for example, one may titrate to the first deviation from the alkaline color (p_T about 5.8) or to the acid color (p_T about 4.8).

It should be noted that the excess of alkali given refers to water that is free from carbon dioxide; when the neutral solution is in equilibrium with carbon dioxide from the air the excess of alkali necessary is about twice as great if phenolphthalein or thymolphthalein is used as indicator.

The most suitable amounts of various indicators to be used in micro titrations have been studied by Mika.[19] He regards specifications based only upon the quantity for a certain volume of solution as insufficient, preferring to take into account also the thickness of the layer through which one looks. Therefore he expresses the indicator addition in milligrams per square centimeter, that is, as the product of the layer depth in centimeters times the concentration in milligrams per cubic centimeter. He recommends additions corresponding to 0.0065 mg. per sq. cm. for methyl red, 0.026 for phenolphthalein and 0.08 for bromothymol blue.

4. Standard Solutions for Acidimetry and Alkalimetry.—Solutions of fairly accurately known content may easily be prepared from concentrated acids of reagent quality and from strong solutions of alkalies, on the basis of specific gravity. This method was long ago recommended by Marshall[20] and several convenient tables have been prepared for this purpose.[21] Schoorl[22] carried out very accurate investigations of the common acids and sodium hydroxide; his values can be used for the exact preparation of standard solutions. In order to attain an accuracy of 0.1%, the mass per unit volume must be known to within 0.0001 unit at a temperature $t° \pm 0.1°$C. Once this is determined, dilution can be made by taking a weighed amount of the solution, without regard for small temperature changes. In order to simplify the calculation, Schoorl expressed the concentrations on a weight–normality basis, that is, in equivalents of acid or base per kilogram of solution. These are listed in the tables under N_W; the corresponding densities at 15.0°C. are given under d_{15} (d_{15} = sp. gr. 15°/4° in vacuum). For convenience in interpolating, the differences between successive figures in these columns are shown under Δ. The temperature coefficient of the density, that is, the change in density per degree centigrade, is given under $\Delta d/\Delta t$.

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[19] J. Mika, *Mikrochemie*, **9**, 143 (1931), **10**, 384 (1932); *cf.* A. A. Benedetti-Pichler and S. Siggia, *Ind. Eng. Chem., Anal. Ed.*, **14**, 828 (1942).

[20] A. Marshall, *J. Soc. Chem. Ind.*, **18**, 4, 1091 (1899), **21**, 1511 (1902).

[21] F. W. Küster *et al.*, *Chem.-Ztg.*, **26**, 1055 (1902), *Ber.*, **38**, 150 (1905); E. C. Worden and J. Motion, *J. Soc. Chem. Ind.*, **24**, 178 (1905).

[22] N. Schoorl, *Chemisch Jaarboekje der Nederlandsche Chemische Vereeniging*, Vol. II, 15th ed., Centen, Amsterdam 1930, p. 94.

Illustration: A hydrochloric acid solution is found to have a density of 1.10013 at 16°C. Therefore the density at 15° is $1.10013 + 0.00045 = 1.10058$, and $N_W = 5.4884 + \left(\frac{111}{518} \times 0.2744\right) = 5.5472$. To prepare a liter of 0.1 N solution one weighs out $\frac{1000 \times 0.1}{5.5472} = 18.927$ g. and dilutes with water to 1000 ml.

Values given in the tables are restricted in each case to the concentration ranges which are most favorable for accuracy and within which there is no danger of concentration changes during weighing in an ordinary weighing bottle.

Stock Solutions of Hydrochloric Acid: Aqueous solutions of hydrochloric acid are entirely satisfactory as standard solutions for alkalimetry. In many laboratories sulfuric acid is preferred, especially for titrations of hot liquids or when it is necessary to boil the sample with an excess of acid. Dilute hydrochloric acid may be used equally well in these cases; 0.1 N solutions are capable of being boiled for an hour without loss of acid if the evaporated water is continually replaced. Even 0.5 N acid may be boiled about 10 minutes without appreciable loss.

Various methods have been proposed for the preparation of hydrochloric acid solutions of known concentrations. Chief among these are the direct addition of dry hydrogen chloride to water until a

WEIGHT NORMALITY AND DENSITY AT 15°C. OF SEVERAL SOLUTIONS, ACCORDING TO SCHOORL[22] (see footnote 22 on p. 63)

%	d_{15}	Δ	$\Delta d/\Delta t$	N_W	Δ
Hydrochloric Acid (Equivalent Weight 36.440)					
19	1.09431	—	0.00043	5.2140	—
20	1.09947	516	0.00045	5.4884	0.2744
21	1.10465	518	0.00046	5.7628	0.2744
22	1.10986	521	0.00047	6.0372	0.2744
23	1.11511	525	0.00048	6.3117	0.2745
24	1.12040	529	0.00049	6.5861	0.2744
25	1.12573	533	0.00050	6.8605	0.2744
Sulfuric Acid[23] (Equivalent Weight 49.013)					
25	1.1810	—	0.00065	5.101	—
26	1.1890	80	0.00066	5.305	0.204
27	1.1970	80	0.00067	5.509	0.204
28	1.2051	81	0.00068	5.713	0.204
29	1.2132	81	0.00069	5.917	0.204
30	1.2213	81	0.00070	6.121	0.204
31	1.2295	82	0.00071	6.325	0.204
32	1.2377	82	0.00071	6.529	0.204
33	1.2460	83	0.00072	6.733	0.204
34	1.2544	84	0.00073	6.937	0.204
35	1.2628	84	0.00073	7.141	0.204
36	1.2712	84	0.00073	7.345	0.204
37	1.2797	85	0.00074	7.549	0.204
38	1.2883	86	0.00074	7.753	0.204
39	1.2969	86	0.00074	7.958	0.205
40	1.3056	87	0.00075	8.162	0.204
41	1.3144	88	0.00075	8.366	0.204
42	1.3233	89	0.00075	8.570	0.204
43	1.3323	90	0.00076	8.774	0.204
44	1.3413	90	0.00076	8.978	0.204
45	1.3504	91	0.00077	9.182	0.204
Nitric Acid (Equivalent Weight 62.975)					
25	1.15056	—	0.00065	3.9698	—
26	1.15728	672	0.00067	4.1286	0.1588
27	1.16400	672	0.00069	4.2874	0.1588
28	1.17072	672	0.00071	4.4462	0.1588
29	1.17745	673	0.00073	4.6050	0.1588
30	1.18418	673	0.00075	4.7638	0.1588
31	1.19091	673	0.00077	4.9226	0.1588
32	1.19764	673	0.00079	5.0814	0.1588
33	1.20436	672	0.00081	5.2402	0.1588
34	1.21107	671	0.00083	5.3990	0.1588
35	1.21777	670	0.00085	5.5578	0.1588
36	1.22446	669	0.00087	5.7166	0.1588
37	1.23113	667	0.00089	5.8754	0.1588

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[23] Purity tests for sulfuric acid and several values for the specific gravity at 25°/25°C. are given by H. W. Conroy, *J. Assoc. Official Agr. Chem.*, **25**, 664 (1942).

WEIGHT NORMALITY—*Continued*

Nitric Acid (Equivalent Weight 62.975)—*Continued*

%	d_{15}	Δ	Δd/Δt	N_W	Δ
38	1.23779	666	0.00091	6.0341	0.1587
39	1.24442	663	0.00093	6.1929	0.1588
40	1.25103	661	0.00095	6.3517	0.1588
41	1.25762	659	0.00097	6.5105	0.1588
42	1.26418	656	0.00099	6.6693	0.1588
43	1.27071	653	0.00101	6.8281	0.1588
44	1.27721	650	0.00103	6.9869	0.1588
45	1.28367	646	0.00105	7.1457	0.1588

Sodium Hydroxide (Equivalent Weight 39.988)

%	d_{15}	Δ	Δd/Δt	N_W	Δ
15	1.1665	—	0.00050	3.7511	—
16	1.1776	111	0.00050	4.0012	0.2501
17	1.1887	111	0.00051	4.2513	0.2501
18	1.1997	110	0.00052	4.5013	0.2500
19	1.2108	111	0.00053	4.7514	0.2501
20	1.2218	110	0.00054	5.0015	0.2501
21	1.2329	111	0.00055	5.2516	0.2501
22	1.2439	110	0.00056	5 5017	0.2501
23	1.2548	109	0.00057	5.7517	0.2500
24	1.2658	110	0.00058	6.0018	0.2501
25	1.2768	110	0.00058	6.2519	0.2501
26	1.2877	109	0.00059	6.5020	0.2501
27	1.2986	109	0.00059	6.7521	0.2501
28	1.3094	108	0.00060	7.0021	0.2500
29	1.3202	108	0.00060	7.2522	0.2501
30	1.3309	107	0.00060	7.5023	0.2501

certain increase in weight has occurred, and the distillation of strong acid in order to obtain a constant-boiling solution.

Raschig[24] gave the following procedure for direct addition: About 90 ml. of water is placed in a 100 ml. volumetric flask, a capillary tube (long enough to reach the bottom and bent to a right angle at the top) is inserted, and the assembly is weighed on an analytical balance. Then the flask is placed on a good tare balance sensitive to 0.01 g. and the capillary tube is connected with a Kipp generator through 30 cm. of small diameter rubber tubing. The generator is charged with small lumps of ammonium chloride from which dry hydrogen chloride is liberated by the action of concentrated sulfuric acid. The flask is tared with the tube hanging free, then hydrogen chloride is led in until the weight increase amounts to 3.7 g. After removal of the rubber tube the flask is reweighed accurately; from the gain in weight one calculates the concentration which the acid will have upon dilution to 100 ml.

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[24] F. Raschig, *Z. angew. Chem.*, **17**, 578 (1904); see also G. T. Moody, *J. Chem. Soc.*, **73**, 658 (1898); W. A. Roth, *Z. angew. Chem.*, **17**, 716 (1904); S. P. L. Sörensen and A. C. Andersen, *Z. anal. Chem.*, **44**, 179 (1905); S. F. Acree and R. F. Brunel, *Am. Chem. J.*, **36**, 117 (1906); H. Rebenstorff, *Chem.-Ztg.*, **32**, 99 (1908).

Hulett and Bonner[25] recommended the use of a constant-boiling mixture. The concentration of this is dependent upon the pressure under which it is distilled. Foulk and Hollingsworth[26] made a very careful study, taking into account the air buoyancy and determining the hydrogen chloride concentrations with atomic weight technique. According to them, one starts with hydrochloric acid of sp. gr. 1.18 and distills at a rate of 3–4 ml. per minute. (The rate has but little influence on the composition of the distillate; upon very slow distillation the acidity of the distillate increases a little.) After about three-fourths of the original solution has gone over, the constant-boiling fraction is collected until a residue of not less than 50–60 ml. remains. Therefore it is advisable to start with about a liter of solution; by taking acid of sp. gr. 1.103 initially, however, about three-fourths of the distillate can be utilized.

The barometer is read to within 1 mm. and the "equivalent weight" of the distillate is found with the aid of the accompanying table. In this way one can easily obtain a standard solution accurate to within 0.05%. If the distillation is carried out at 760 mm., then 18.019 g. are diluted to 1000 ml. to prepare an exactly 0.1 N solution. The distillate should be kept in a tightly stoppered flask.

COMPOSITION OF CONSTANT-BOILING HYDROCHLORIC ACID[27]

(Foulk and Hollingsworth)

Pressure during Distillation, mm. Hg	HCl Content, (vacuum conditions), %	Rational Equivalent Weight of Solution (in Air), g. per mole of HCl
730	20.293	179.55
740	20.269	179.77
750	20.245	179.98
760	20.221	180.19
770	20.197	180.41
780	20.173	180.62

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[25] G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.*, **31**, 390 (1909).

[26] C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).

[27] On the basis of these and other data, an equation for the air weight of constant boiling hydrochloric acid required for one equivalent has been devised by W. H. King, *J. Assoc. Official Agr. Chem.*, **25**, 653 (1942):

$$G = \frac{P + 7680}{46.8386}$$

where G is the air weight in grams and P is the barometric pressure in millimeters of mercury corrected to 0°C. The equation is said to give values accurate to within one part per thousand at pressures between 540 and 780 mm.

The compositions of constant-boiling hydrochloric acid solutions at various pressures have also been determined carefully by Bonner and his co-workers.[28] Values shown in the accompanying table have been taken from the data of Bonner and Wallace.

COMPOSITION OF CONSTANT-BOILING HYDROCHLORIC ACID

(Bonner and Wallace)

Pressure, mm. Hg	Boiling Point, °C.	Density, 25°C.	HCl, %
600	102.21	1.0980	20.638
640	103.97	1.0973	20.507
680	105.56	1.0968	20.413
700	106.42	1.0966	20.360
740	107.86	1.0962	20.268
760	108.58	1.0959	20.222
800	110.01	1.0955	20.155

Stock Solutions of Perchloric Acid: Smith and Koch[29] suggested the use of 73.6% perchloric acid, which is constant-boiling under 3.5 to 5 mm. pressure.

Pure 72% acid is distilled at 2–7 mm. in an all-glass apparatus until half of the volume has come over (if 71% acid is taken, three-fifths are distilled over). Then a clean dry receiver is attached and a fraction collected while

DENSITY OF AQUEOUS PERCHLORIC ACID

(Goehler and Smith)

$HClO_4$, %	d_{25}	Δ	Rational Equivalent Weight of Solution (in Air), g. per mole $HClO_4$	Δ
65.00	1.59665	—	154.50	—
66.00	1.61016	0.01351	152.16	2.34
67.00	1.62367	0.01351	149.87	2.29
68.00	1.63718	0.01351	147.68	2.19
69.00	1.65060	0.01342	145.54	2.14
70.00	1.66420	0.01360	143.46	2.08
71.00	1.67763	0.01343	141.44	2.02
72.00	1.69106	0.01343	139.48	1.96
73.00	1.70449	0.01343	137.57	1.91
74.00	1.71790	0.01341	135.71	1.86
75.00	1.73125	0.01335	133.90	1.81

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[28] W. D. Bonner and B. F. Branting, *J. Am. Chem. Soc.*, **48**, 3093 (1926); W. D. Bonner and A. C. Titus, *ibid.*, **52**, 633 (1930), W. D. Bonner and R. E. Wallace, *ibid.*, **52**, 1747 (1930). See also J. A. Shaw, *Ind. Eng. Chem.*, **18**, 1065 (1926), A. C. Titus and D. E. Smith, *J. Am. Chem. Soc.*, **63**, 3266 (1941).

[29] G. F. Smith and W. W. Koch, *Ind. Eng. Chem., Anal. Ed.*, **3**, 52 (1931); Smith and O. E. Goehler, *ibid.*, **3**, 48 (1931).

the pressure is held within the above limits. The temperature may vary between 60° and 95°C. depending upon the distillation rate. The useful fraction contains 73.60 ± 0.03% $HClO_4$ and has a density of 1.71282 ± 0.00004 at 25°. Since the acid is slightly hygroscopic and fumes in the air, it should be stored in a well-stoppered flask and protected against the entrance of moisture during weighing. For the preparation of a normal solution 136.45 g. are diluted to 1000 ml. with water.

Goehler and Smith[30] have determined accurately the densities at 25° C (sp. gr. 25°/4° in vacuum) of various strengths of perchloric acid between 65 and 75% $HClO_4$ by weight. In the preceding table are given some of their results, together with calculated values of the number of grams required for preparing one liter of normal acid (rational equivalent weight of the solution).

The densities of several less concentrated perchloric acid solutions were determined by Markham,[31] some of whose results are given below. Attention is called to the fact that Markham's density for 65% acid is a little lower than that of Goehler and Smith.

$HClO_4$, %	d_{25}	$HClO_4$, %	d_{25}
20.00	1.12280	50.00	1.39937
30.00	1.20002	55.00	1.46134
40.00	1.29073	60.00	1.52766
45.00	1.34252	65.00	1.59628

Stock Solutions of Alkalies: Sodium hydroxide is generally employed in standard alkaline solutions, though potassium and barium hydroxides have their uses. If the solution must be kept free from carbonate, barium hydroxide treated with barium chloride or nitrate may be selected; the neutral barium salt diminishes the solubility of barium carbonate. Barium hydroxide solutions must be protected carefully or their titers will decrease through carbonate formation; partly on this account they cannot be recommended highly for general work. The same is true of the other alkalies, solutions of which easily absorb carbon dioxide from the atmosphere especially when hot. While strongly alkaline liquids are cooling they take up carbon dioxide avidly.

Strong alkaline solutions kept in containers of ordinary glass are likely to become contaminated with silicates. Paraffined flasks are more suitable for the storage of stock solutions. While silicates have little influence on the titer of the alkali during standardization, they interfere in the carbonate determination of Winkler (p. 108) by forming barium silicate. The latter, however, is only partially precipitated if the alkali is less than 0.05 N.

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[30] O. E. Goehler and G. F. Smith, *Ind. Eng. Chem., Anal. Ed.*, **3**, 61 (1931).
[31] A. E. Markham, *J. Am. Chem. Soc.*, **63**, 874 (1941).

Glass-stoppered vessels are not suitable for storage of stock alkalies, although sticking of the stoppers may be lessened by greasing with vaseline or paraffin. Cork stoppers soon soften and go to pieces. Metal stoppers of phosphor bronze, silvered phosphor bronze, or pure nickel are very good.[32] Rubber stoppers, though not entirely satisfactory, are generally used.

Exposure of the alkaline solution to carbon dioxide from the air should be avoided by the use of a closed system for the burette and supply bottle, such as that shown on page 14.

Since the preparation of practically carbonate-free solutions of sodium or potassium hydroxide is relatively simple, it is generally unnecessary to work with barium hydroxide. Commercial sodium hydroxide "purified with alcohol" contains only a little carbonate; with quick handling and rinsing off of the outer crust one can prepare a solution of which only one or two per cent of the alkali is in the form of carbonate. For accurate analysis, however, this is still too high. Several methods of removing the carbonate are available.

a. Strong Alkali Method of Sörensen:[33] Pure sodium hydroxide is dissolved in an equal weight of water (or 4 parts sodium hydroxide to 5 parts water) by shaking briskly in a rubber-stoppered flask or cylinder. Sodium carbonate is practically insoluble in this strong alkali, and after sufficient time it settles to the bottom. A clear solution can be obtained more quickly by filtering through a sintered glass crucible. According to Allen and Low[34] it is simpler and better to centrifuge the suspension. Han and Chao[35] found (after dilution of the filtered strong alkali to about 1 N with carbon dioxide-free water) that approximately 0.15% of the alkali was present in the form of carbonate. Allen and Low found 0.12% after centrifuging.

The procedure is not applicable for the preparation of carbonate-free potassium hydroxide, for potassium carbonate is appreciably soluble.

b. Lime Method of Kolthoff:[36] One first prepares an approximately 1.1 N solution of reagent-grade sodium or potassium hydroxide. To one liter is added 50–80 ml. of milk of lime and the mixture is shaken mechanically for an hour, then allowed to stand for several days before the clear liquid is siphoned off. Carbon dioxide is kept out with a soda–lime tube. After dilution to 0.1 N the solution contains at most 1 or 2 mg. of calcium per liter.

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[32] F. Michel, *Chem.-Ztg.*, **37**, 634 (1913). Stoppers of ebonite are recommended by A. van Raalte, *Chem. Weekblad*, **25**, 528 (1928).

[33] S. P. L. Sörensen, *Biochem. Z.*, **21**, 168 (1909). A similar procedure is given by H. W. Cowles, Jr., *J. Am. Chem. Soc.*, **30**, 1192 (1908). The authors do not know which method is the earlier.

[34] N. Allen and G. W. Low, Jr., *Ind. Eng. Chem., Anal. Ed.*, **5**, 192 (1933).

[35] J. E. S. Han and T. Y. Chao, *ibid.*, **4**, 229 (1932); see also J. E. S. Han, *ibid.*, **6**, 209 (1934), **9**, 140 (1937).

[36] I. M. Kolthoff, *Z. anal. Chem.*, **61**, 48 (1922).

Calcium hydroxide is slightly soluble in water (about 0.0234 M at 18°C.) but the solubility is greatly diminished in the presence of strong alkali. In a solution saturated with both calcium hydroxide and calcium carbonate, the mass law expression is:

$$[Ca^{++}] = \frac{S_{Ca(OH)_2}}{[OH^-]^2} = \frac{S_{CaCO_3}}{[CO_3^=]}$$

or

$$[CO_3^=] = \frac{S_{CaCO_3}}{S_{Ca(OH)_2}} [OH^-]^2 = 3 \times 10^{-4} [OH^-]^2$$

Therefore one calculates that in a 1 N solution of alkali the carbonate concentration would be about 3×10^{-4} M, or that about 0.06% of the alkali would be in the form of carbonate. On the contrary, Han and Chao[35] found that in a solution of 1.1 N sodium hydroxide so prepared about 1% of the alkali was present as carbonate. Possibly the solubility products in strong alkali differ from those used in the above calculation. Han and Chao found lower carbonate contents after treatment with strontium or barium hydroxides, but more of these compounds remain in the final solution. If the presence of an alkaline earth is not objectionable, therefore, one may advantageously substitute barium for calcium in the lime method. Otherwise, the strong alkali method is to be preferred.

The testing of an alkali solution for carbonate is simple. One fills a test tube one-fifth full of 0.5 N barium nitrate (or chloride) and the rest of the way with the alkali, then stoppers quickly and shakes. No turbidity of barium carbonate should appear within 10 minutes. The carbonate content may easily be determined by titration with standard acid to phenolphthalein and to methyl yellow (pp. 109, 132).

Dilution Water: Most texts specify the use of boiled and cooled distilled water for preparing 0.1 N solutions of alkali. In principle this is correct, yet the purpose is served equally well by using water which is in equilibrium with the carbon dioxide of the air. Such water is only 1.5×10^{-5} M in carbon dioxide[37]; if a 0.1 N solution is diluted to 0.01 N with it, only 0.3% of the alkali will be transformed into carbonate. Ordinary distilled water may contain ten times as much carbon dioxide, which escapes very slowly upon aeration. Equilibrium with the air may be reached after a week of standing open (but protected from dust), or much more rapidly by bubbling with air that has been washed with acid and water. A 500 ml. portion of the aerated water treated with 5 drops of 1% phenolphthalein ought not to require more than 0.1 ml. of 0.1 N alkali before showing a red color. The p_H should be greater than 5.7.

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[37] I. M. Kolthoff, *Biochem. Z.*, **176**, 101 (1926).

c. Alcohol Method: Various authors[38] dissolve the sodium or potassium hydroxide first in alcohol, in which the corresponding carbonates are insoluble, and dilute the clear solution with water. This procedure has no advantage over *a* (so far as the sodium hydroxide solution is concerned) or over *b* in either case.

d. Preparation from the Metal: For physicochemical purposes such as conductivity measurements, in which the carbonate-free alkali should also be free from chloride, sulfate or other impurities, solutions of commercial alkalies are generally not satisfactory. One may prepare relatively pure solutions from the metals, though some trouble is involved and one must guard against explosions.

Suitable procedures have been given by Küster[39] and by Bousfield and Lowry.[40] Stahl[41] described an improved apparatus in which 25 g. of sodium can be converted into the hydroxide in 11–12 hours. One can also prepare strong pure alkali by electrolysis of the chloride in a mercury cell (*cf.* Jorrissen and Izu[42]).

It is more convenient, however, to use purchased potassium hydroxide or sodium hydroxide of the highest purity such as that prepared from the metal ("e natrio" in the latter case). This is obtainable free from chloride and sulfate and can easily be made carbonate-free by Sörensen's method.

Alcoholic Alkalies: Carbonate-free alcoholic solutions of sodium or potassium hydroxide, such as are used in the determination of saponification number, are readily prepared since the alkali carbonates are insoluble in alcohol. A disadvantage of various alcoholic alkali solutions is that on standing they turn yellow or brown, meanwhile forming salts of organic acids and decreasing in titer. M. Kitt[43] has shown that the discoloration arises from the presence of aldehydes in the alcohol, so that purification of the latter is desirable.

By following the directions of the United States Pharmacopoeia it is possible to prepare solutions that remain colorless for a period of several years. One dissolves 2 g. of silver nitrate in 5 ml. of distilled water, adds this to 1200 ml. of alcohol in a glass-stoppered flask and mixes carefully.

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[38] *Cf.* C. Winkler, *Praktische Übungen in der Massanalyse,* 3rd ed., Leipzig 1902.

[39] F. W. Küster, *Z. anorg. Chem.*, **13**, 134 (1897), **41**, 474 (1904); A. Harpf and H. Fleissner, *Z. chem. Apparatenkunde,* **1**, 534 (1906); F. W. Küster, *ibid.*, **1**, 535 (1906); *Chem. Zentr.* **1906**, 994.

[40] W. R. Bousfield and T. M. Lowry, *Phil. Trans.*, **204**, 253 (1905). See also J. Cornog, *J. Am. Chem. Soc.*, **43**, 2573 (1921).

[41] W. Stahl, *Z. anal. Chem.*, **97**, 86 (1934).

[42] W. P. Jorrissen and H. F. Izu, *Z. angew Chem.*, **23**, 726 (1910). See also W. M. Clark, *The Determination of Hydrogen Ions,* 3rd ed., Williams & Wilkins, Baltimore 1928, p. 197.

[43] M. Kitt, *Z. anal. Chem.*, **46**, 533 (1907).

Then 5 g. of potassium hydroxide are dissolved in 25 ml. of warm alcohol and the mixture is cooled and added to the alcoholic silver nitrate solution. The precipitated silver oxide is allowed to settle out, the solution is filtered, and the alcohol is distilled off. For preparing a 0.5 N alkali solution one dissolves 35 g. of potassium hydroxide in 20 ml. of distilled water and dilutes to a liter with the purified alcohol. The solution is mixed and kept stoppered overnight, then is decanted quickly into a brown glass bottle with rubber stopper.

The method of Malfatti[44] has been recommended by Valyashko.[45] In the presence of a little alcohol the required amount of potassium hydroxide is triturated with an equal or somewhat greater amount of calcium oxide. The paste is washed into a flask with alcohol and made to the desired volume. After shaking until all the potassium hydroxide is dissolved, the suspension is allowed to settle and the clear solution is decanted off or filtered.

5. The Standardization of Acids.—Acid solutions are usually standardized against pure reference substances, general specifications for which have been given in Chapter II. The individual standards are described in more detail later in this section. There are, however, several methods of standardizing acids without the use of a primary substance. Some of these are given below.

Residue Method: Köszegi[46] suggested a procedure in which an accurately weighed or measured quantity of the acid (hydrochloric or sulfuric) is exactly neutralized with sodium or potassium hydroxide and the solution is evaporated to dryness in a tared porcelain dish on the steam bath. The residue is weighed after drying at 120°C. and cooling. In order to keep the crystal layer thin and thus minimize the retention of moisture, a flat shallow dish is used. Water of decrepitation is always present, but under suitable conditions its content is so low as to be negligible. The procedure is naturally subject to interference by impurities in either the acid or the alkali, the latter being especially difficult to obtain in a sufficiently pure state. From a practical standpoint the method does not appear to have much importance, particularly if one works with dilute solutions.

Coulometric Method: Szebellédy and Somogyi[47] standardize acids, sodium hydroxide, and thiocyanate with the aid of a silver coulometer, measuring the quantity of electricity which is necessary to electrolyze the solutions completely. For the electrolysis of hydrochloric acid they employ a platinum cathode and a silver anode; when all the acid is decomposed the solution becomes neutral and if a neutral salt is present continued electrolysis produces alkali. The end-point is shown by an indicator and a comparison solution. It is claimed that results accurate to within 0.01% are possible.

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[44] H. Malfatti, *Z. anal. Chem.*, **50**, 692 (1911); *Chem. Abstracts*, **6**, 200 (1912).

[45] N. Valyashko, *Farm. Zhur.*, **1928**, p. 34; *Chem. Abstracts*, **23**, 4647 (1929).

[46] D. Köszegi, *Z. anal. Chem.*, **111**, 343 (1938).

[47] L. Szebellédy and Z. Somogyi, *Z. anal. Chem.*, **112**, 313, 323, 332, 385, 395 (1938).

For the standardization of sulfuric acid, an alkali chloride is added to the solution and silver chloride forms at the anode. The standardization of sodium hydroxide is more complicated. One adds alkali bisulfite and bromide, then electrolyzes until the originally alkaline solution reaches the p_H of a pure bisulfite solution. During electrolysis the liberated bromine oxidizes bisulfite to bisulfate, which reacts strongly acid and neutralizes the original alkali.

To standardize thiocyanate solution, bromide is added. At the anode bromine reacts with thiocyanate to form sulfuric, hydrocyanic and hydrobromic acids. The end-point is shown by the persistence of a yellow bromine color.

PRIMARY SUBSTANCES FOR ACID STANDARDIZATION

Sodium Oxalate ($Na_2C_2O_4$, equivalent weight 67.01, rational 66.99): Sörensen[48] recommended sodium oxalate as an ideal primary standard both for acids and for permanganate. The salt is not hygroscopic and may easily be obtained free from water of crystallization.

In order to purify the salt, according to Sörensen, one dissolves it in water, makes the solution slightly alkaline and allows it to stand until insoluble impurities such as calcium oxalate settle out. After filtration the clear liquid is evaporated to one-tenth of its volume, whereupon sodium oxalate crystallizes. Potassium oxalate and similar impurities remain in solution. The sodium oxalate is filtered out, pulverized, and washed several times with water. The process is repeated until the final mother liquor is clear, free from sulfate, and practically neutral to phenolphthalein.

Two crystallizations from water are generally sufficient. The solubility of sodium oxalate is about 34 g. per liter at 20° and 62 g. per liter at 100°C. Glassware low in calcium should be used, otherwise calcium oxalate may be formed in the hot solution. Sodium oxalate preparations meeting Sörensen's specifications are available from the United States Bureau of Standards and from several commercial firms.

Upon heating the oxalate to form sodium carbonate (p. 77), the crystals easily burst. Therefore it has been suggested that the more voluminous form obtained by precipitating a warm saturated solution with alcohol is better. According to Schoorl the alcohol precipitation is superfluous if one dries the salt at 240°C. before transforming it into carbonate.

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[48] S. P. L. Sörensen, *Z. anal. Chem.*, **36**, 639 (1897), **42**, 333, 512 (1903). S. P. L. Sörensen and A. C. Andersen, *ibid.*, **44**, 156 (1905), **45**, 217 (1906).

Tests for Purity: Sodium oxalate commonly encloses some water which cannot be removed completely by heating to 150°C. Sörensen found that an anhydrous product can be obtained by heating for several hours at 240–250°, without danger of decomposition. If the oxalate is then kept in air the surface condensation of moisture is negligible (less than 1:10,000). This trace of moisture may be removed by drying at 100°; according to Schoorl about 0.01% is again taken up quickly on exposure to air. Investigations at the Bureau of Standards[49] have shown that small crystals, obtained by disturbed crystallization from water and dried at 240°, take up 0.01% water from an atmosphere of 70% relative humidity. Under the same conditions the more voluminous alcohol-precipitated product adsorbs 0.04% water.

Test for Hygroscopic Moisture:[50] 10 g. of sodium oxalate, weighed in a weighing bottle with tightly fitting stopper, should not lose more than 1 mg. (0.01%) upon drying for 24 hours in an oven at 100°C.

Test for Water of Decrepitation: 5 g. is placed in a clean narrow test tube which has previously been heated and cooled, and the tube is allowed to stand for a few hours in a drying oven at 90 to 100°C. The warm tube is closed with a cork stopper fitted with a small calcium chloride tube, and is allowed to cool. Upon careful heating of the lower part of the tube over a free flame, no trace of moisture should condense in the upper part. Sensitivity 0.01% H_2O.

Test for Calcium: The solution of 3 g. in 100 ml. should show no turbidity of calcium oxalate.

Test for Potassium: 0.5 g. of sodium oxalate is converted into carbonate by heating moderately and is taken up in 5 ml. of water and filtered. The filtrate is treated with 5 ml. of 4 N acetic acid, 1 ml. of de Koninck's reagent (p. 81) and 10 ml. of 96% alcohol. No turbidity of potassium sodium cobaltinitrite should appear within 5 minutes; sensitivity 0.04% $K_2C_2O_4$.

Potassium oxalate is an active impurity, 0.1% lowering the effective strength of sodium oxalate by 0.02%.

Tests for Other Inorganic Impurities: 10 g. of the salt in a platinum crucible on an asbestos ring is decomposed over a flame. The carbonate formed is dissolved in 50 ml. of 4 N acetic acid (free from chloride) and the solution is filtered. Half of the filtrate treated with silver nitrate should show no more turbidity than a solution containing 0.25 mg. of chloride in the same volume. The other half should give no test for sulfate on treatment with barium nitrate. This portion can also be tested for iron and aluminum by neutralizing with ammonia to methyl red. The solution should remain clear after standing for two hours on a steam bath; sensitivity 0.003% Fe_2O_3 or Al_2O_3.

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[49] *Sodium Oxalate as a Standard in Volumetric Analysis,* Bureau of Standards Circular No. 381 (1930).

[50] S. P. L. Sörensen, *Z. anal. Chem.*, **42**, 513 (1903).

In another 10 g. portion of the salt after complete ignition and conversion to chloride one may test for insoluble matter, for iron (with thiocyanate or ammonium sulfide) or for potassium as above.

Test for Organic Impurities: A clean test tube is heated to redness and cooled, then 1 g. of the sodium oxalate and 10 ml. of pure, dust-free, concentrated sulfuric acid are introduced and heated, gently while the gas is given off and finally more strongly until the acid begins to boil. After cooling, the color is compared with that of a blank which has been treated in the same way. No more than a very pale brownish tint should be imparted to the acid.

Tests for Alkaline or Acid Impurities (carbonate, bicarbonate, or bioxalate): These impurities are all active in acidimetry. The presence of 0.1% Na_2CO_3 raises the effective strength by only 0.02%, while the same quantity of $NaHCO_3$ lowers it by 0.025% and of $NaHC_2O_4$ by 0.067%.

Because of hydrolysis a pure solution of sodium oxalate reacts weakly alkaline. Taking the second ionization constant K_2 of oxalic acid as 4.5×10^{-5} and assuming that the activity coefficient of the anion in a 0.1 M sodium oxalate solution is 0.7, one can calculate that:

$$[H^+] \text{ at } 18°\text{C.} = 2.0 \times 10^{-9},\ p_H = 8.7$$
$$[H^+] \text{ at } 25°\text{C.} = 2.7 \times 10^{-9},\ p_H = 8.57$$

In order to determine the p_H of a pure sodium oxalate solution, the water must be free from carbonic acid and atmospheric carbon dioxide must be excluded.

Sörensen gave a lengthy test for finding carbonate or bioxalate, which has been criticized by Blum[51] because no allowance was made for the possible presence of bicarbonate. According to Blum's experiments, sodium bicarbonate present in sodium oxalate is not completely decomposed upon heating to 240°C. Blum therefore gave a procedure in which 200 ml. of water with 0.2 ml. of 1% phenolphthalein is evaporated to 150 ml. in quartz or Durax glass, in a stream of pure air free from carbon dioxide; 4 g. of sodium oxalate is then added. Boiling is continued for 10 minutes, after which the solution is cooled to room temperature while the air stream is still maintained. The solution is finally titrated with 0.01 N alkali or acid to a p_T of 8.6. Each milliliter of alkali required corresponds to 0.04% $NaHCO_3$ or 0.03% $NaHC_2O_4$.

According to Blum, Jena glass is not satisfactory because the oxalate decomposes and the solution becomes strongly alkaline. On the contrary, Kolthoff observed that a *pure* concentrated sodium oxalate solution can be boiled for two minutes in Jena glass without any perceptible alteration of the p_H. He found that the test can be made more simply as follows: 60 ml. of water containing 2 drops of 1% phenolphthalein is boiled for 2 minutes in a Jena or Pyrex glass flask, then 2 g. of sodium oxalate is added and the solution is boiled a minute longer. A soda-lime tube is immediately connected with the flask and the latter is cooled to room temperature. If the solution is colored, it is titrated to colorless with 0.01 N acid; if colorless, it is titrated to a rose color with 0.01 N alkali.

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[51] W. Blum, *J. Am. Chem. Soc.*, **34**, 123 (1912). A modification of Blum's procedure is given in Bureau of Standards Circular No. 381 (1930).

The solution ought not to consume more than 0.5 ml. of 0.01 N acid or 0.4 ml. of 0.01 N alkali (equivalent to about 0.023% sodium bioxalate).

Entirely pure sodium oxalate after treatment as described above yields a solution that is barely alkaline to phenolphthalein and requires 0.3 ml. of 0.01 N acid for decoloration. A Kahlbaum preparation (Sörensen's method), which had apparently not been heated to 240°C, was found to take only 0.15 ml. of 0.01 N acid and therefore contained less than 0.01% of bioxalate.

Bicarbonate, if present, is not completely decomposed under the given conditions. For its determination the solution is boiled and if the titration exceeds 0.5 ml. of 0.01 N acid, an additional boiling period of one minute is allowed. The solution is then cooled as before and the titration is completed. This procedure is repeated until the red color fails to appear after boiling and cooling. Each ml. of 0.01 N acid corresponds to 0.84 mg. of sodium bicarbonate. In this way a standard sample from the Bureau of Standards was shown to contain 0.13% bicarbonate; it was therefore to be rejected as a primary substance, especially for standardizing permanganate. Generally a single boiling test is sufficient. If more than 0.5 ml. of 0.01 N acid is consumed the preparation is unreliable. Good lots contain no bicarbonate and at most only a trace of bioxalate.

Conversion of Sodium Oxalate into Sodium Carbonate: According to Sörensen[50] the accurately weighed material is carefully heated in a partly covered platinum crucible for 15 to 30 minutes over a small gas flame or alcohol lamp. Lunge[52] states that, if illuminating gas is used, the crucible should be placed in an inclined asbestos board to protect the contents from sulfur dioxide. The crucible is first heated, with the cover on, for 15 minutes over a very small flame, and then more strongly with the lid halfway off until the carbon burns off and the sodium carbonate begins to melt. A part of the sodium carbonate may be decomposed to oxide, but this does no harm provided the temperature does not become high enough to volatilize any of the oxide.

Procedure for Standardization, According to Sörensen: Somewhat more acid than corresponds to the weighed amount of oxalate is measured out from a burette into a tall beaker. The cooled crucible is treated with a little water and is set upright in the beaker of acid, the cover also being placed therein. After the carbonate has become sufficiently moistened to prevent any loss of powder during the reaction, the beaker is covered with a glass and tilted to allow acid to enter the crucible. When all of the sodium carbonate has been dissolved and the greater part of the carbon dioxide expelled by heating on a water bath, the solution is transferred to an Erlenmeyer flask and the crucible, cover, beaker, and glass are all rinsed well with water. Several drops of phenolphthalein are added, the carbon dioxide is completely driven out by boiling, and after cooling under a tap the excess of acid is titrated with a standardized solution of sodium hydroxide. The titration error is practically negligible.

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[52] G. Lunge, *Z. angew. Chem.*, **17**, 230 (1904).

The authors prefer to perform the titration as follows: The carbonate solution is titrated using methyl orange as indicator. When the color has become distinctly red (p_H about 3), a drop of a freshly prepared dilute solution of bromine is added to discharge the methyl orange color. The solution is boiled for a few minutes to remove carbon dioxide. After cooling, the slight excess of acid is back-titrated with 0.01 N sodium hydroxide to a color change of methyl red or bromothymol blue. The end-point is sharp and no indicator correction is needed. The use of such a dilute solution for back-titrating minimizes the error involved in the final burette readings.

In several polemic publications Lunge[53] has warmly recommended direct titration of the carbonate with acid, using methyl orange as indicator. In this case the titration error (*cf.* p. 151) must be taken into account. Another difficulty is that a saturated solution of carbon dioxide containing sodium chloride, such as is present at the end-point, shifts the methyl orange color appreciably toward the acid side. Because of this, too little acid is consumed in titrating to the first perceptible color change. Küster[39] observed this long ago and therefore proposed titration to the "normal color," *i.e.*, until the color matches that of a reference solution saturated with carbon dioxide and containing as much indicator and sodium chloride as the titrated solution. By such means one may obtain practically exact, although perhaps not strictly exact, results. During titration there is formed a supersaturated solution of carbonic acid, but on shaking near the equivalence-point more or less carbon dioxide is lost and the solution becomes unsaturated; it is therefore difficult to maintain identical conditions in the two solutions.

For most practical purposes the following procedure gives satisfactory results in the standardization of acids that are 0.1 N or stronger: The carbonate solution is titrated using methyl yellow or methyl orange until the color begins to deviate from the water tint. At this stage the equivalence-point has not yet been reached. The solution is boiled for two minutes, or warmed for 15 minutes on the water bath with occasional shaking; it then contains very little carbonic acid. After cooling it is titrated until the color is barely different from the water color of the indicator. From the volume of acid used, the *working titer referred to methyl yellow* is calculated.

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[53] G. Lunge, *Z. angew. Chem.*, **18**, 1520 (1905).

If one wishes to apply a correction for the titration error, this may be determined in a separate experiment. A reference solution, composed of the same quantities of distilled water, indicator and sodium chloride as would be present in the titrated solution at the equivalence-point, is titrated with acid until the color matches that of the titrated solution. At room temperature the correction amounts to about 0.1 ml. of 0.1 N acid per 100 ml. One can also boil out all of the carbon dioxide after the methyl orange change (5 minutes of boiling, or half an hour on the steam bath), and after cooling titrate with alkali until an orange color is shown using phenolphthalein. The difference between the quantities used with methyl yellow and with phenolphthalein should not exceed 0.15 ml. of 0.1 N acid per 100 ml. of liquid.

Titrations of carbonate with acid may be carried out directly in hot solution using bromothymol blue or phenol red. The end-points are sharp and free from titration error, back-titrations are avoided and no reference solutions are necessary. The disadvantages are those involved in the handling of the heated solution (protection of the burette from temperature changes, possible attack of the vessel by hot carbonate, etc.), and the fact that the titration is a little tedious.

The carbonate is carefully dissolved in a little water in a quartz or platinum dish or pyrex glass flask. Two drops of indicator are added and then somewhat less than the expected quantity of acid. Next the solution is boiled until the alkaline color returns, to expel most of the carbon dioxide, and the boiling solution is titrated carefully with small portions of acid. Protection from the flame is secured by placing the dish in an asbestos board with a round hole. After each addition of acid the alkaline color disappears but may return after a few minutes of heating. Toward the end, fractions of a drop are removed from the burette tip by means of a quartz or platinum spatula and are transferred to the solution. When the color no longer returns after 3 minutes, the titration is complete.

OTHER STANDARD SUBSTANCES

The most popular standard substances for acids are sodium carbonate and borax.

Sodium Carbonate (Na_2CO_3, equivalent weight 53.00, rational 52.99): The preparation of pure anhydrous sodium carbonate is very simple; in view of this fact and the cheapness of the starting material, the use of purified sodium carbonate as a primary standard has been strongly recommended by G. Lunge. Chemically pure soda may be bought upon the market, tested for purity and used after drying at 270 to 300°C. Alternatively one may start with crude soda, filter the saturated solution and precipitate sodium bicarbonate by passing in carbon dioxide. The bicarbonate is washed with water and tested for chloride and sulfate. Quite pure sodium bicarbonate, usually contaminated with only a little carbonate, is commercially available. The conversion into sodium carbonate is simple (see below).

In the procedure of Reinitzer,[54] 250 ml. of water is heated to 80°C. in a beaker of resistant glass, and powdered bicarbonate is added with stirring until no more dissolves. During this time carbon dioxide is evolved. The solution is filtered through a folded filter, best in a jacketed funnel, and is cooled to 10–15°. The coarsely crystalline salt which separates is a mixture of bicarbonate and trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. After decantation of the mother liquor, the crystals are drained by suction and washed with distilled water.

Conversion of Sodium Bicarbonate into Carbonate; Dehydration: Bicarbonate is quantitatively transformed into carbonate by heating to 270–300°C., according to Lunge[55]; at the same time the preparation becomes anhydrous.

About 10 g. of sodium bicarbonate is placed in a porcelain or (preferably) a platinum crucible and spread out with a spoon to give a uniform layer. The crucible is then heated for half an hour to an hour at 270–300°C. in a sand or air bath or electric oven. With the aid of a short platinum wire, which is kept in the crucible, the soda is stirred continually during the heating. This prolonged stirring is unquestionably necessary, especially if a larger amount of the standard is being prepared at one time.[56] After the heating, the crucible and contents are cooled in a desiccator. Large quantities should be kept in a vessel with a tight glass stopper, or may be divided among several such containers in order that as little exposure to the air as possible should occur when portions are withdrawn.

Lunge's thorough investigations indicated that at the specified temperatures no decomposition of sodium carbonate to oxide takes place, although such an effect had previously been reported in the literature[57] and the controversy still continues. From a careful study Lindner and Figala[58] concluded that a product heated to 300°C. does not contain free sodium oxide. Waldbauer, McCann, and Tuleen[59] found that bicarbonate is completely converted to carbonate by heating to 150°. The heating of anhydrous sodium carbonate may be carried to as high as 375° without decomposition, but in all cases in which sodium bicarbonate was used as starting material the effective strength of the product was found to be about 0.1% high. This was ascribed to transformation of a little bicarbonate to oxide or hydroxide during the early stages of heating (it takes place even at 165°), but the mechanism is not yet clear. Washing the sodium carbonate with alcohol and drying it at 110° appears to remove the oxide; products so prepared gave results agreeing with the theoretical, within an experimental error of about 0.03%.

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[54] B. Reinitzer, *Z. angew. Chem.*, **7**, 551 (1894).

[55] G. Lunge, *Z. angew. Chem.*, **10**, 522 (1897), **17**, 231 (1904), **18**, 1520 (1905).

[56] *Cf.* H. Kunz-Krause and R. Richter, *Arch. Pharm.*, **255**, 540 (1917); *J. Chem. Soc.*, **116**, II, 423 (1919).

[57] C. L. Higgins, *J. Soc. Chem. Ind.*, **19**, 958 (1900); S. P. L. Sörensen and A. C. Andersen, *Z. anal. Chem.*, **44**, 156 (1905); J. Sebelien, *Chem.-Ztg.*, **29**, 638 (1905); B. North and W. Blakey, *J. Soc. Chem. Ind.*, **24**, 396 (1905); K. O. Schmitt, *Z. anal. Chem.*, **70**, 321 (1927).

On the other hand, Smith and Croad[60] claim that above 300°C. sodium carbonate decomposes with evolution of carbon dioxide. After heating for an hour at 310–315° they obtained an effective alkalinity 1% too large, with markedly increasing values at higher temperatures. While the authors have not been able to confirm these results, it appears safe to recommend that the heating be carried out at lower temperatures, or in a stream of carbon dioxide.

Tests for Purity—Chloride: Upon dissolving 0.5 g. of sodium carbonate in 10 ml. of 2 N nitric acid (chloride-free) and adding 5 ml. of 0.1 N silver nitrate, no more opalescence should appear than is obtained with 10 ml. of a 1 N nitric acid solution containing 5 mg. of sodium chloride per liter and treated with the same amount of silver nitrate. Sensitivity 0.01% NaCl.

Sulfate: A solution of 0.5 g. of sodium carbonate in 10 ml. of 2 N acetic acid, treated with barium nitrate, should give no turbidity or precipitate of barium sulfate after standing 15 minutes. Sensitivity 0.01% Na_2SO_4.

Potassium: A solution of 0.5 g. of the carbonate in 10 ml. of 2 N acetic acid, treated with 1 ml. of de Koninck's sodium cobaltinitrite reagent[61] and 10 ml. of alcohol, should show no turbidity after standing for 5 minutes. Sensitivity 0.04% K_2CO_3.

Potassium carbonate is an active impurity; 0.1% lowers the effective strength of sodium carbonate by 0.023%.

Sodium Hydroxide: Sörensen and Andersen[62] give a procedure in which 200 ml. of water containing a little phenolphthalein is evaporated to about 100 ml. in an Erlenmeyer flask of resistant glass, while air free from carbon dioxide is continuously passed through the flask. To the hot water is added

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[58] J. Lindner and N. Figala, *Z. anal. Chem.*, **91**, 105 (1933).

[59] L. Waldbauer, D. C. McCann, and L. F. Tuleen, *Ind. Eng. Chem., Anal. Ed.*, **6**, 336 (1934).

[60] G. F. Smith and G. F. Croad, *ibid.*, **9**, 141 (1937). The data in this paper appear inconsistent, in that the error in effective alkalinity as observed volumetrically is about ten times as great as that calculated from the weight of carbon dioxide lost upon heating for one hour at 310–315°C.

[61] de Koninck's reagent: (*a*) Dissolve 50 g. of crystallized cobalt nitrate in a liter of water and acidify with 40 ml. of 4 N nitric acid. (*b*) Dissolve 300 g. of crystallized sodium nitrite in a liter of water. Add solution (*a*) to (*b*) with stirring, let stand for 24 hours and filter out any precipitate.

[62] S. P. L. Sörensen and A. C. Andersen, *Z. anal. Chem.*, **45**, 217 (1906).

2 g. of sodium carbonate and as soon as it dissolves about 8 g. of barium chloride is introduced, while the air stream is still maintained. If after thorough shaking and cooling under the tap the mixture is red, it is titrated with 0.1 N hydrochloric acid to colorless.

The test may be made more simply as follows: 30 ml. of water is boiled for 2 minutes in a resistant flask, then 2 g. of the sodium carbonate is added and the flask is closed with a soda-lime tube. Immediately after solution the hot liquid is treated with 25 ml. of 20% barium chloride, the flask is shaken and cooled under protection of the soda-lime tube, and 2 drops of 1% phenolphthalein are added. If the solution is colored, it is titrated to colorless with 0.01 N hydrochloric acid. (The precipitation must be carried out in hot solution, since otherwise a little barium bicarbonate is occluded and the liquid becomes alkaline to phenolphthalein even though the original sodium carbonate may have been pure.) The titration should not exceed 1 ml. of 0.01 N acid, equivalent to 0.02% sodium hydroxide. This alkali is an active impurity; 0.1% increases the effective strength by 0.032%.

According to Schmitt[63] the above procedures are not suitable for indicating small proportions of hydroxide (0.1% or less). In the author's experience the simplified method gives reliable results, although there may be some coprecipitation of basic salt with the barium carbonate according to LeBlanc[64] and Schmitt; an adsorption of indicator by the precipitate also seems to occur.

Water and Sodium Bicarbonate: About 10 g. is weighed quickly in a platinum crucible, then heated for an hour at 300° C., cooled in a desiccator and again weighed rapidly (weights already on the balance). The loss in weight should not amount to more than 1 mg. (0.01%). One can also test directly for water by Sörensen's method as has been described under sodium oxalate, p. 75.

Insoluble Matter: A solution of 5 g. of sodium carbonate in 25 ml. of water should be entirely clear.

The Standardization of a Strong Acid against Sodium Carbonate: The calculated quantity, weighed in a covered crucible or weighing bottle is dissolved in water and titrated with acid, either using phenolphthalein as indicator and boiling out the carbon dioxide, or directly using methyl orange. Details are the same as those given on p. 78 for converted sodium oxalate. In order to avoid spattering of the liquid by effervescence, acid is first added in the usual way until phenolphthalein is decolored; then with the flask inclined, a somewhat smaller quantity is allowed to flow down the wall, without shaking until all has been introduced. Alternatively a funnel may be placed in the flask and washed off shortly before the end-point.

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[63] K. O. Schmitt, *Z. anal. Chem.*, **70**, 321 (1927).

[64] M. LeBlanc, *Z. anorg. Chem.*, **53**, 344 (1907).

Titration of the heated solution using bromothymol blue or phenol red, as previously described, is also quite accurate.

Sodium carbonate has, inconveniently, the property of being hygroscopic and even taking up moisture during weighing. This was pointed out long ago by Sebelien[65] and has been confirmed by Sörensen and Andersen as well as by Kolthoff.[66] Sebelien found upon weighing 6 g. of soda in a platinum crucible a gain of 4 mg. or 0.07%, although the relative humidity was only 24%. Kolthoff noted an increase of 1–3 mg. while weighing 2.65 g. in a weighing bottle. An error of 0.1% may easily arise, especially in weighing out the small quantity of soda that is needed for standardizing 0.1 N acid.

Thallous Carbonate (Tl_2CO_3, equivalent weight 234.40, rational 234.38): Hac and Kamén[67] recommend thallous carbonate as a primary standard. It is easily prepared by metathesis of thallous nitrate with sodium carbonate or with methylammonium carbonate and alcohol, or by treatment of thallous hydroxide with carbonic acid.

Thallous carbonate is sparingly soluble in water (solubility 5.3 g. in 100 g. water at 18°C., 27.2 g. at 100°) and can easily be purified by recrystallization. The yield may be increased by cooling in ice and adding alcohol. The salt crystallizes (without water of hydration) in colorless needles which after being powdered and dried at 90–110° are practically nonhygroscopic. After storing the product in an atmosphere saturated with water vapor, Hac and Kamén found a moisture content of only 0.017%. No decomposition was noted upon heating to 175°, nor was any occluded water detected by Sörensen's qualitative test.

Jensen and Nilssen[68] recommend that the final crystallization be made from platinum, since hot concentrated solutions of thallous carbonate attack glass. Both pairs of authors give directions for testing the purity of the product.

Tests for Purity—Water: Upon heating a 10 g. portion to 175°C. the weight should not decrease by more than 1 mg. (0.01%).

Insoluble Matter:[68] 0.5 g. should give a perfectly clear solution in 5 ml. of hot water. Sensitivity 0.01% Mg, Ca, Ba, Al, Fe, Mn, Pb.

Copper:[67] Upon dissolving 1 g. in 50 ml. of dilute acetic acid and testing with potassium ferrocyanide no colored precipitate should appear. Sensitivity 0.002%.

Bismuth:[67] 2 g. of the salt is neutralized to methyl orange with nitric acid, boiled to expel carbon dioxide, and diluted to 50 ml. with water. The precipitate produced by addition of a thiourea solution should be pure white; bismuth is indicated by a yellow or brown color sensitive to 0.002%.

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[65] J. Sebelien, *Chem.-Ztg.*, **29**, 638 (1905).

[66] I. M. Kolthoff, *Pharm. Weekblad*, **63**, 37 (1926).

[67] R. Hac and K. Kamén, *Collection Czechoslov. Chem. Commun.*, **4**, 145 (1932). See also a note by A. J. Berry, *Analyst*, **64**, 27 (1939).

[68] E. Jensen and B. Nilssen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 508 (1939).

Alkalies:[67] A solution of 1 g. of the salt is neutralized with hydrochloric acid, precipitated with hydrogen sulfide and filtered. After evaporation of the filtrate, the residue should not weigh more than 0.2 mg. (0.02%). Jensen and Nilssen eliminate thallium from a 5 g. sample by oxidizing with bromine and precipitating with ammonium hydroxide, then they evaporate the filtrate, expel ammonium salts, and determine the loss in weight of the residue upon extraction with hot water. The loss should not exceed 0.5 mg. (0.01%). Tests for potassium with cobaltinitrite (p. 81) and for sodium with zinc uranyl acetate might be found simpler and more sensitive.

Nitrate:[68] Boil 0.5 g. with 1 ml. of water, cool and mix with an excess of a 1% solution of diphenylamine in concentrated sulfuric acid. No coloration should appear; sensitivity $<0.01\%$.

Chloride and Sulfate: See tests of sodium carbonate, p. 81.

The Standardization of Acids against Thallous Carbonate: The weighed amount of pure material is dissolved in water in a resistant flask, treated with methyl orange and titrated with acid to the first change from the water color. Carbon dioxide is boiled out, the solution is cooled and the titration is carried on to the end-point. In a corresponding volume of water the indicator correction is determined. For details and optional procedures *cf.* standardizations against sodium carbonate, p. 78.

During titration with hydrochloric acid a white precipitate of thallous chloride separates, but redissolves on heating. Since the precipitate is sensitive to sunlight, turning violet and liberating a little chlorine which destroys the indicator, the titration should be performed in diffuse light.

Sodium Bicarbonate ($NaHCO_3$, equivalent weight 84.01, rational 83.98): This substance was proposed as a primary standard by North and Blakey.[69] Although Lunge's investigations[70] indicated that it is not satisfactory, Schoorl (private communication) found it to be stable in air and quite useful.

Potassium Bicarbonate ($KHCO_3$, equivalent weight 100.11, rational 100.07): According to the vapor pressure measurements of Caven and Sand,[71] the carbon dioxide pressure from dissociation of potassium bicarbonate is lower than that from sodium bicarbonate at the same temperature. Therefore potassium bicarbonate has an advantage over the sodium salt.

Lüning[72] pointed out that as long ago as 1839 Ure mentioned potassium bicarbonate as a standard in his *Dictionary of Arts.* The salt was tested and strongly recommended by von Than.[73] Winkler[74] established that preparations which have been saturated with carbon dioxide and dried over sulfuric acid show an effective strength averaging about 0.04% low. Incze[75] obtains the salt by passing carbon dioxide into alcoholic potassium hydroxide, dissolving the crystals in water, and reprecipitating with alcohol; this product possesses the theoretical activity. According to Incze potassium bicarbonate has the advantages of containing no water of crystallization, of being nonhygroscopic and therefore weighable without special precautions, of having a high equivalent weight, and of being readily available.

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[69] B. North and W. Blakey, *J. Soc. Chem. Ind.*, **24**, 396 (1905). See also J. W. Young, *Can. J. Research*, **B17**, 192 (1939).

[70] G. Lunge, *Z. angew. Chem.*, **18**, 1520 (1905).

[71] R. M. Caven and H. J. S. Sand, *J. Chem. Soc.*, **99**, 1359 (1911), **105**, 2752 (1914).

[72] O. Lüning, *Chem.-Ztg.*, **42**, 5 (1918).

In contradiction, Bruhns[76] maintains that in atmospheres of relative humidity greater than 70% the salt attracts water. He also notes that larger crystals of a commercial C.P. product were found to be 0.32% below strength because of enclosed mother liquor. This may be remedied by powdering the crystals and keeping the powder in dry air until the weight becomes constant. In this process the mother liquor evaporates and any potassium carbonate which it may have contained is converted into bicarbonate by the atmospheric carbon dioxide. Potassium bicarbonate in fine crystals is adequate for ordinary standardizations. Bruhns makes use of the flame test for detecting impurities; traces of sodium appear as a yellow color which may mask the potassium flame, while calcium and lithium colors remain after all the potassium is volatilized so that these elements may be recognized with the naked eye or with the aid of a spectroscope.

Schmitt,[77] who studied both the sodium and potassium salts, recommends recrystallization of the latter from water. Carbon dioxide is continuously passed into 250 ml. of water at 65–70°C.—no higher—and 200 g. of analytical grade potassium bicarbonate is added with stirring. The solution is filtered and reheated to dissolve any crystals which form in the receiver during filtration, then it is cooled to 15° with ice while the carbon dioxide is still passed through and the mixture is stirred. The crystals are collected on a Buchner funnel, sucked dry, washed twice with distilled water, and dried in the air. Finally the salt is pulverized, dried again to constant weight, and transferred to a tightly stoppered bottle. The salt crystallized from water is more coarse than that obtained by alcohol precipitation as in Incze's method. Schmitt obtained excellent results with his product.

Kolthoff and Sandell[78] followed Schmitt's procedure but dried the salt over sulfuric acid in a carbon dioxide atmosphere. They found this product to give values agreeing to within 0.02% of those obtained with pure borax, sodium carbonate, and a potassium bicarbonate prepared according to Incze's directions. Potassium bicarbonate can therefore be highly recommended as a primary standard.

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[73] C. von Than, *Math. naturw. Ber. Ungarn*, **6**, 127 (1889).

[74] L. W. Winkler, *Z. angew. Chem.*, **28**, 264 (1915).

[75] G. Incze, *Z. anal. Chem.*, **54**, 585 (1915).

[76] G. Bruhns, *Chem.-Ztg.*, **41**, 386 (1917), **42**, 5 (1918), **48**, 89 (1924).

[77] K. O. Schmitt, *Z. anal. Chem.*, **70**, 321 (1927).

[78] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **3**, 115 (1931).

Bruhns[76] transforms the bicarbonate into carbonate by igniting gently over a small flame for 10 to 15 minutes in a platinum crucible. During the heating the crucible is kept partly covered, then the lid is replaced while the crucible is cooled in a desiccator and weighed *rapidly*. Potassium carbonate is very hygroscopic; ignition and weighing should be repeated until the weight is constant.

According to Schmitt[77] potassium bicarbonate in finely crystalline form suffers no weight loss at 90–100°C. At 200–210° it is completely converted to carbonate in two hours. A peculiarity observed by both Schmitt and the senior author is that upon further heating at higher temperature a slight increase in weight is found. The quantity of carbon dioxide lost is always slightly greater than that calculated stoichiometrically. Because of these phenomena and the hygroscopic character of the product, potassium carbonate cannot be recommended for standardizations.

Calcite: Various writers[79] have attempted to use calcite, or other forms of calcium carbonate, for standardizing acids. Thiele and Richter[80] found deviations of up to 0.2% from the theoretical value when using calcite. Another disadvantage is that the material must be dissolved in an excess of acid and titrated back with standard alkali.

Potassium Bitartrate: This substance has been recommended as a standard by Bornträger.[81] It is converted into potassium carbonate by ignition prior to being used for standardizing an acid. The advantage that it may also be employed in alkali standardizations is offset by the difficulty encountered in trying to test its purity accurately.

Borax ($Na_2B_4O_7 \cdot 10H_2O$, equivalent weight 190.72, rational 190.60): Borax was early suggested as a primary standard and has since been recommended by a number of investigators,[82] in whose opinions the authors concur.[83] The compound may be obtained pure on the market or may easily be purified by recrystallizing from water (solubility 3 g. per 100 ml. at 25°C., 54 g. at 90°). It is stable under the proper storage conditions, does not absorb moisture during weighing, and has a high equivalent weight. The standardization of an acid may be carried out very simply (more so than with sodium carbonate, and at least as accurately). Borax may also be used for standardizing alkalies. The main disadvantage of borax as a standard is that thorough tests of its purity are difficult to perform.

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[79] *Cf. Z. anal. Chem.*, **2**, 426 (1863); G. Lunge and E. Berl, *Chemisch-technische Untersuchungsmethoden*, 7th ed., Springer, Berlin 1922, Vol. 1, p. 132; G. Calcagni and M. Starnajolo, *Ann. chim. applicata*, **22**, 16 (1932); J. W. Young, *Can. Chem. Met.*, **18**, 218 (1934).

[80] H. Thiele and R. Richter, *Z. angew. Chem.*, **13**, 486 (1900).

[81] A. Bornträger, *Z. anal. Chem.*, **31**, 56 (1892).

[82] E. Rimbach, *Ber.*, **26**, 171 (1893); T. Salzer, *ibid.*, **26**, 430 (1893); *Z. anal. Chem.*, **32**, 529 (1893); W. Worm, *Z. anal. Chem.*, **36**, 688 (1897); H. D. Richmond, *Chem. News*, **72**, 5 (1895); E. P. Perman and W. John, *ibid.*, **71**, 296 (1895); E. Rupp, *Chem.-Ztg.*, **31**, 97 (1907); M. T. Milobedzki and H. Kaminska, *Bull. soc. chim.*, **41**, 957 (1927); N. A. Lasarkewitsch, *Ukraïn. Khem. Zhur.* (Scientific Part), **4**, 405 (1929), *cf. Z. anal. Chem.*, **81**, 45 (1930).

[83] *Cf.* I. M. Kolthoff, *Pharm. Weekblad.*, **63**, 37 (1926); I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **3**, 115 (1931).

Borax may be prepared from pure boric acid (tested for completeness of volatility with methanol and hydrochloric acid) and an equivalent amount of pure sodium carbonate, or a good commercial preparation may be crystallized three times from water. The crystals are quickly freed from most of the mother liquor by suction and are finally dried to constant weight in an atmosphere of 70% relative humidity. This is conveniently maintained in a desiccator (hygrostat) containing a solution saturated with both sodium chloride and sucrose, in the presence of an excess of each solid.[84] Exposure of the moist salt to air should be avoided because it takes up a little carbon dioxide and thus becomes contaminated with carbonate or bicarbonate. Such contamination is difficult to detect, a gravimetric determination of the carbon dioxide liberated by acid being the best available test.

Hurley[85] crystallizes the borax below 55°C. (to ensure formation of the decahydrate) and washes twice with water, twice with alcohol, and twice with ether. The remaining ether is allowed to evaporate in air. After the weight has become constant the product can be kept in well closed bottles. However, if the stopper does not close tightly efflorescence may occur, so that it is safer to use the hygrostat. Good results according to Hurley's method are reported by Vandaveer.[86]

The theoretical water content of borax is 47.22%. Water may be determined by drying a weighed quantity in a platinum crucible first on a steam bath, then further at about 200°C., and finally in an electric muffle at 700–800°. The last molecule of water is very difficult to drive out. If the borax has been prepared properly and kept in a hygrostat, the water determination is unnecessary.

Tests for Purity:[87]—*Insoluble Substances:* A solution of 5 g. of the salt in 45 ml. of water should be clear and colorless. Sensitivity about 0.01%.

Chloride: A 10% solution should not show with nitric acid and silver nitrate any more turbidity than a solution containing 5 mg. of chloride per liter. Sensitivity 0.005%.

Sulfate: A 10% solution treated with acetic acid and barium nitrate should not yield any precipitate after standing half an hour. Sensitivity 0.01%.

Calcium: A 10% solution heated to boiling with ammonium oxalate should not show any turbidity after cooling. Sensitivity 0.01%.

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[84] H. Menzel, *Z. anorg. allgem. Chem.*, **224**, 1 (1935).

[85] F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.*, **8**, 220 (1936), **9**, 237 (1937).

[86] R. L. Vandaveer, *J. Assoc. Official Agr. Chem.*, **22**, 563 (1939).

[87] N. Schoorl, *Commentaar op de Nederlandsche Pharmacopee*, 5th ed., Oosthoek, Utrecht 1927, p. 352. Schoorl also gives more exact tests for calcium, silica, carbon dioxide, aluminum and sulfate.

Magnesium: A 5% solution should not give any microcrystalline precipitate after standing for 24 hours with diammonium phosphate and ammonium hydroxide. Sensitivity 0.002%.

Potassium: 5 ml. of a 5% solution treated with 1 ml. of 4 N acetic acid, 5 ml. of sodium cobaltinitrite reagent (p. 81), and 5 ml. of alcohol should not become turbid.

Water Content: 10 g. of borax dried and melted as described previously should lose 4.722 ± 0.001 g. Each milligram of deviation from this figure corresponds to 0.01% deficiency or excess of moisture.

Standardization of Acids with Borax: The standardization of 0.1 N hydrochloric acid against borax can be done without any titration error if methyl red is employed as indicator. A reference solution is used with just as much boric acid, sodium chloride, and indicator as the titrated solution contains at the equivalence-point. If, for example, one starts with 0.762 g. of borax, corresponding to about 40 ml. of 0.1 N hydrochloric acid, and dissolves it in 40 ml. of water, then the reference liquid should consist of 80 ml. of a solution 0.1 M in boric acid and 0.05 M in sodium chloride. Under these conditions the end-point with methyl red can be recognized to within 0.01 ml.

Methyl yellow or methyl orange may also be used as indicator. Although in the titration of sodium carbonate one must allow for the disturbing effects of liberated carbon dioxide (p. 78), the borax titration proceeds very sharply to the end-point. There is always a small titration error corresponding to the excess of acid which is necessary to change the indicator. In titrating to the first deviation from the water color, the error amounts to about 0.07 ml. of 0.1 N acid per 100 ml. of solution. It is better to use methyl yellow or methyl orange instead of methyl red in standardizing acids that are stronger than 0.2 N. Here also one should use an appropriate reference solution, for stronger solutions of boric acid react slightly acid to these indicators. Nevertheless the end-points can be perceived within an accuracy of 0.01 ml.

Note: According to Baggesgaard-Rasmussen and Christensen,[88] a borax solution is much less sensitive to atmospheric carbon dioxide than is sodium hydroxide, and therefore has an advantage for many titrations such as those of ammonium or alkaloid salts.

Potassium Iodate (KIO_3, equivalent weight 35.67, rational 35.66): Potassium iodate may be obtained commercially in pure condition, the product of Kahlbaum being suitable without further purification, or it may be prepared by recrystallizing technical material two or three times from water and drying at 150–180°C. It is then entirely anhydrous and may be kept without danger of absorbing moisture. The compound is an excellent standard for thiosulfate solutions;

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[88] H. Baggesgaard-Rasmussen and C. E. Christensen, *Dansk Tids. Farm.*, **1**, 65 (1926); *Chem. Abstracts*, **21**, 215 (1927).

after reduction to iodide it may also be used for standardizing permanganate,[89] ceric sulfate or silver nitrate. In standardizing an acid one makes use of the reaction:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

If a neutral iodate solution is treated with an excess of neutral iodide and thiosulfate and then titrated with acid, hydrogen ions are removed until all iodate has been reduced to free iodine as in the above equation. The liberated iodine is simultaneously reduced by the excess of thiosulfate:

$$I_2 + 2S_2O_3^{=} \rightarrow 2I^- + S_4O_6^{=}$$

Meanwhile the solution remains neutral, because tetrathionic acid is a strong electrolyte, and colorless as well, since the products are colorless. As soon as all of the iodate has been used up, any additional acid introduced remains in the solution and may be revealed with an indicator.

Standardization of a Strong Acid against Potassium Iodate:[90] The potassium iodide and sodium thiosulfate to be used must react neutral and must not consume any acid with methyl yellow as indicator. A solution of 4 g. of potassium iodide in 10 ml. of water should give a transition shade to methyl yellow after addition of a drop of 0.1 N acid. Ten grams of sodium thiosulfate in 10 ml. of water should show the transition tint after addition of 0.1 ml. of 0.1 N acid. Good reagent grade products meet these requirements; impure preparations must be purified by recrystallization.

In standardizing 0.1 N hydrochloric acid the most suitable indicators are methyl red, methyl yellow, bromocresol green or bromophenol blue. For 100 mg. of potassium iodate there should be allowed 150 mg. of potassium iodide and 800 mg. of sodium thiosulfate. These need not be weighed out accurately but a large excess of thiosulfate should be avoided because it causes the change to be less sharp. By titrating to a p_T of 5 (methyl red) the titration error is minimized. A disadvantage is that the red color appears and then fades in the vicinity of the equivalence-point since the reaction proceeds with measurable velocity. After each addition of acid one must wait for several seconds, and at the end-point for three minutes, to see whether the color change is permanent.

The titration can be carried directly to the end-point with the other indicators mentioned. In any case the solution should be shaken thoroughly while acid is being added, in order to prevent decomposition of thiosulfate by local excesses. About 0.1 ml. too much of 0.1 N acid is required if the end-point is taken at the first deviation from the water color. The necessary correction should be determined experimentally and subtracted. After the end-point has been reached, further color changes upon standing are inconsequential since the thiosulfate decomposes in acid solution. Nevertheless under good conditions the standardization against potassium iodate is as accurate as that against borax, sodium carbonate or sodium oxalate. The only real drawback is the small equivalent weight of the compound.

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[89] I. M. Kolthoff, *Z. anal. Chem.*, **64**, 255 (1924). R. Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922), **142**, 229, 279 (1925), **144**, 75 (1925).

[90] I. M. Kolthoff, *Pharm. Weekblad*, **63**, 37 (1926).

Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, equivalent weight 248.19, rational 248.04): Bicskei[91] dissolves an accurately weighed quantity of pure sodium thiosulfate crystals in distilled water, treats with an excess of potassium iodate, iodide and starch solution, and titrates with the acid to a permanent blue color. In standardizing 0.1 N acid he uses 2 ml. of 4% potassium iodate and 0.3 to 0.5 g. potassium iodide with 0.5 g. thiosulfate. The purification and testing of thiosulfate will be described in Volume III.

Mercuric Oxide (HgO, equivalent weight = rational weight = 108.30): The yellow oxide of mercury has been used as a primary standard by various workers.[92] Incze[93] investigated it quite thoroughly; his conclusions, however, were not wholly confirmed by Kolthoff and van Berk.[94]

The advantages of mercuric oxide are its high equivalent weight and the facts that it contains no water of crystallization, is not hygroscopic, and can be kept unchanged. With it acids can be standardized as well to phenolphthalein as to methyl yellow (p. 92); furthermore it may be used for the standardization of thiocyanate solutions.

For the preparation of mercuric oxide one pours a solution of 100 g. pure mercuric chloride in a liter of water into 650 ml. of 1.5 N sodium hydroxide, with stirring. In this way the formation of a basic chloride is avoided. The yellow precipitate is washed with water only until the washings no longer react alkaline to phenolphthalein. With extended washing colloidal mercuric oxide passes through the filter (peptization). The product is dried to constant weight by very gentle warming—not over 40°C.—or better in a vacuum desiccator that contains concentrated sulfuric acid, and is kept in a dark place. The finished preparation should be stored in a dark bottle.

[91] J. Bicskei, *Z. anal. Chem.*, **88**, 414 (1932).

[92] See, for example, R. Philip, *Z. ges. Schiess-u. Sprengstoffw.*, **7**, 109 (1912); *Chem. Zentr.* **1912**, **II**, 874. L. Rosenthaler and A. Abelmann, *Pharm. J.*, **37**, 144 (1913); *Z. anal. Chem.*, **53**, 608 (1914); **57**, 98 (1918). E. Biilmann and K. Thaulow, *Bull. soc. chim.*, **29**, 587 (1921).

[93] G. Incze, *Z. anal. Chem.*, **56**, 177 (1917), **57**, 176 (1918).

[94] I. M. Kolthoff and L. H. van Berk, *ibid.*, **71**, 339 (1927).

Commercial products such as are used for pharmaceutical purposes are not sufficiently pure to be employed in standardizations. On the other hand a Kahlbaum sample was found by Kolthoff and van Berk to have the same activity as two of their own preparations. These showed 99.9% of the theoretical strength against acid and only 99.75% against thiocyanate. Tests of the products did not succeed in establishing the presence of significant impurities except for a trace of water.

Tests for Purity: One should not rely on mercuric oxide without making purity tests, although many of the earlier workers have neglected this precaution.

Nonvolatile Substances: On igniting 5 g. mercuric oxide in a weighed porcelain dish (hood!), not more than 0.5 mg. of residue should be left, corresponding to 0.01% nonvolatile matter. The products mentioned above contained about this much.

Water: On drying 5 g. over sulfuric acid in a vacuum desiccator the weight loss should not exceed 0.5 mg. or 0.01%. Although according to Incze the oxide is not hygroscopic, the fine powder may adsorb water on its surface. Air-dried preparations have shown a moisture content of 0.04%.

Chloride: One gram of mercuric oxide is boiled for one minute in 10 ml. of water in which 0.5 g. chloride-free sodium carbonate has been dissolved, and the suspension is filtered. The filtrate, which usually contains a trace of mercuric oxide, is acidified with nitric acid. After addition of 1 ml. of 0.1 N silver nitrate no turbidity should appear. Sensitivity 0.005% Cl.

The oxide should not be dissolved directly in nitric acid and tested, for mercuric ions bind the chloride and the latter easily escapes detection under these conditions.

Insoluble Matter: The solution of 3 g. in 10 ml. of 4 N nitric acid ought to be completely clear and free from any trace of precipitate. This test includes any free mercury that may have been produced by photochemical decomposition.

Standardization of Acids against Mercuric Oxide: Incze makes use of the fact that mercuric ions react with an excess of iodide ions to form a complex:

$$Hg^{++} + 4I^- \rightleftarrows HgI_4^=$$

When mercuric oxide is dissolved in potassium iodide solution, an equivalent quantity of potassium hydroxide is produced:

$$HgO + 2KI + H_2O \rightleftarrows HgI_2 + 2KOH$$
$$HgI_2 + 2KI \rightleftarrows K_2HgI_4$$

Potassium mercuric iodide is colorless and quite soluble. The original procedure of Incze required considerable potassium iodide (about 7 or 8 g. per 0.5 g. of mercuric oxide) and furthermore allowed some absorption of carbon dioxide by the alkali so that an error might occur in titrating to phenolphthalein. Therefore the procedure has been modified by the substitution of potassium bromide for iodide and by the use of a soda-lime tube to prevent absorption of carbon dioxide. Mercuric ions form with bromide a complex similar to that with iodide; although the bromide complex is somewhat less stable, this has no effect on the standardization.

The potassium bromide (or iodide, if one follows Incze's method) must also be tested for acidity or alkalinity. A solution of 20 g. of the salt in 50 ml. of water should show an intermediate color with methyl yellow after addition of one drop of 0.1 N hydrochloric acid.

For standardization the required quantity of mercuric oxide is weighed out and placed in a flask of resistant glass. For one gram of the oxide 20 g. of potassium bromide and 25 ml. of water are added, then a soda-lime tube is connected with the flask and the mixture is shaken and warmed for several minutes until all the oxide is dissolved. After cooling and adding several drops of phenolphthalein, one titrates with acid to colorless. At this point a few drops of methyl yellow are introduced and titration is continued to the first deviation from the water color of this indicator. With careful work the difference between the phenolphthalein and methyl yellow end-points should not amount to more than 0.2 ml. of 0.1 N acid per 100 ml. of solution. Since the alkali generally takes up a little carbon dioxide during titration, it is best to base the standardization on the methyl yellow titer. If necessary the titration error may be compensated by a correction.

Lasarkewitsch[82] recommends mercuric oxide for the standardization of acids and thiocyanate solutions. As mentioned above, however, the author's preparations and that of Kahlbaum consumed too little acid by 0.1%.

Sodium Chloride (NaCl, equivalent weight 58.45, rational 58.44): This substance is an excellent standard for silver nitrate (see p. 251). According to Tananaeff[95] it may also be used for the standardization of acids.

The weighed amount of sodium chloride is placed in a platinum crucible and treated with an excess of normal oxalic acid solution. The solution is evaporated to dryness and the residue is ignited to sodium carbonate and titrated with acid as on p. 78. Since hydrochloric acid is more volatile than oxalic, it is displaced by the latter during evaporation and ignition.

Studies by Murawleff[96] indicated that conversion of the sodium chloride into oxalate is not complete, so that the standardization is undependable. However, continued investigations by Tananaeff and Lasarkewitsch[97] showed that under suitable conditions the reaction takes place quantitatively to within 0.1 or 0.2%. It is unlikely that the procedure will find much practical use.

Diphenylguanidine [$(C_6H_5NH_2)_2CNH$, equivalent weight 211.26, rational 211.17)]: Symmetrical diphenylguanidine is a monoacid base, difficultly soluble in water but readily so in alcohol. It has several important commercial uses and is readily available.

According to Carlton[98] the technical product is only about 97% pure and contains 0.25% ash. One purifies it by first extracting with cold toluene and then recrystallizing three times from this solvent (100 g. to 800 ml. of toluene; yield 82%). Carlton recommends the pure substance highly for the standardization of either aqueous or alcoholic solutions of hydrochloric acid, using methyl red or bromophenol blue as indicator. In either case the diphenylguanidine is first dissolved in 50 ml. of alcohol.

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[95] N. A. Tananaeff, *Z. anorg. allgem. Chem.*, **154**, 186 (1926).

[96] L. N. Murawleff, *ibid.*, **165**, 137 (1927).

[97] N. A. Tananaeff and N. A. Lasarkewitsch, *Z. anal. Chem.*, **81**, 117 (1930).

[98] C. A. Carlton, *J. Am. Chem. Soc.*, **44**, 1469 (1922).

Thornton and Christ[99] obtained results about 0.5–0.6% high in standardizing hydrochloric acid against a sample of diphenylguanidine purified according to Carlton's directions. On the other hand, Young[100] purified various lots of material by different methods and obtained good results. The substance cannot be recommended as a standard until adequate tests of its purity are developed.

6. The Standardization of Alkalies.—Solutions of strong bases, like solutions of strong acids, are generally standardized against reference substances which can be prepared in pure condition and whose purity may be confirmed by qualitative tests. Potassium biphthalate, benzoic acid, and oxalic acid are most commonly used. The first two are available from the National Bureau of Standards. All three, as well as a number of other substances which have been proposed, are discussed below. Most of these compounds are weak acids or weak acid salts, so that an indicator changing on the alkaline side, like phenolphthalein, is needed in the titration.

Some confusion may be caused by slight variations in the active purities of certain standard substances reported in the literature at different times. In 1937 the atomic weight of carbon was changed by the International Committee from 12.00 to 12.01, corresponding to an increase of 0.039% in the equivalent weight of potassium biphthalate or of 0.057% in that of benzoic acid. These changes should be considered in comparing data obtained prior to 1937 with values determined more recently. Furthermore, alkali standards are frequently evaluated indirectly against hydrochloric acid which has been standardized gravimetrically as silver chloride. Consequently an improvement in the gravimetric technique is reflected in the active purity of the substance being tested. Thus the benzoic acid supplied by the Bureau of Standards was reported as 99.99% pure by titration in 1937 (Sample 39e) and as 100.03% in 1944 (Sample 39f). The actual difference between these samples in titration against the same alkali is 0.009%, 39f being the stronger.[101] The rest of the difference is accounted for by a positive correction of 0.057% for the atomic weight change and a negative correction of 0.02% for a fusion loss noted on silver chloride during gravimetric standardization of hydrochloric acid.

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[99] W. M. Thornton, Jr., and C. L. Christ, *Ind. Eng. Chem., Anal. Ed.*, **9**, 339 (1937).

[100] J. W. Young, *Can. J. Research*, **B17**, 192 (1939).

[101] G. E. F. Lundell, private communication.

PRIMARY SUBSTANCES FOR ALKALI STANDARDIZATION

Potassium Biphthalate ($KHC_8H_4O_4$, equivalent weight 204.22, rational 204.14): This salt has been recommended by Dodge[102] and by Hendrixson.[103] The product obtainable from the Bureau of Standards (Sample 84b) has an active value of 100.04%. Hendrixson's method of preparing the salt consists in treating pure, sublimed phthalic acid with slightly more than the theoretical quantity of anhydrous potassium carbonate and crystallizing three times from water. The solubility is 12.7% at 35°C. and 36.1% at 100°. The purified compound is dried at 125° but not higher, since sublimation of phthalic anhydride then takes place. After drying, the biphthalate shows not more than 0.003% water; it is not hygroscopic. Products contaminated by potassium phthalate can be purified by crystallization from water. Those containing an excess of free phthalic acid may also be recrystallized, but the crystals should be allowed to separate at a temperature above 35°. According to Smith[104] lower temperatures lead to a product which contains too much acid, through formation of some of the double salt $K_2C_8H_4O_4 \cdot 4H_2C_8H_4O_4 \cdot 4H_2O$.

Kolthoff and Sandell[105] obtained excellent results in the standardization of sodium hydroxide with potassium biphthalate. The salt is also well suited for the standardization of barium hydroxide. If one dissolves the weighed amount of biphthalate in 75 ml. of warm water (40–50°C.) and titrates at this temperature, the results agree with the theoretical. The solution then remains clear during titration. In working at room temperature barium phthalate precipitates toward the end and occludes a trace of barium hydroxide. Kolthoff and Sandell found deviations of 0.05% from the theoretical value under these conditions.

Benzoic Acid (C_6H_5COOH, equivalent weight 122.12, rational 122.07): Benzoic acid was long ago proposed as a standard by

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[102] F. D. Dodge, *Ind. Eng. Chem.*, **7**, 29 (1915).

[103] W. S. Hendrixson, *J. Am. Chem. Soc.*, **37**, 2352 (1915), **42**, 724 (1920).

[104] S. B. Smith, *ibid.*, **53**, 3711 (1931).

[105] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **3**, 115 (1931).

Wagner[106] and has been recommended by Phelps and Weed[107] and especially by Morey.[108] The acid is much used as a standard substance in calorimetry and is available in quite pure form.

Morey crystallizes the commercial product twice from alcohol and once from water, then sublimes it in vacuum. Such a preparation is very fluffy and can be handled better if it is first melted in a platinum vessel at 125–130°C. Surface condensation of moisture on powder obtained by pulverizing the cooled melt is negligible; the acid itself is not hygroscopic.

Procedure for Standardization of 0.1 N Alkali: Weigh out 0.5 g. of pure benzoic acid, dissolve it in 20 ml. of neutral alcohol in an Erlenmeyer flask through which is passed a stream of carbon dioxide-free air, and titrate using phenolphthalein as indicator. Prepare a blank on the same quantity of alcohol and indicator, with sufficient pure water to make the total volume the same as that of the other solution at the end-point, and titrate this to the same color. Subtract the blank as an indicator correction.

Note: The Bureau of Standards recommends titrating a 1 g. sample, but since this requires nearly 80 ml. of alkali it is more convenient for practical work to use a smaller weight.

Oxalic Acid ($H_2C_2O_4 \cdot 2H_2O$, equivalent weight 63.03, rational 63.00): In addition to its use for standardizing alkalies, oxalic acid may also serve for standardizations of permanganate and thiosulfate. As long ago as 1852 the crystallized compound was recommended as a standard by F. Mohr. Its disadvantages are that difficulties are encountered in obtaining the acid with exactly two moles of water per mole and entirely free from salts.[109]

On this account various workers[110] suggested the use of anhydrous sublimed acid. Treadwell and Johner[111] first dehydrate the crystallized acid at 100°C. and then sublime it at 140° in the vacuum of an aspirator pump.

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[106] J. Wagner, *Proceedings of the Fifth International Congress for Applied Chemistry*, Vol. I, Berlin 1903, p. 323.

[107] I. K. Phelps and L. H. Weed, *Am. J. Sci.*, **26**, 138 (1908); *Z. anorg. Chem.*, **59**, 120 (1908).

[108] G. W. Morey, *J. Am. Chem. Soc.*, **34**, 1027 (1912); *cf.* E. R. Weaver, *ibid.*, **35**, 1309 (1913).

[109] *Cf.* H. Thiele and H. Deckert, *Z. angew. Chem.*, **14**, 1233 (1901); H. Habedanck, *Z. anal. Chem.*, **11**, 282 (1872); D. M. Lichty, *J. Phys. Chem.*, **11**, 227 (1907).

[110] W. Hampe, *Chem.-Ztg.*, **7**, 73, 106 (1883), *Z. anal. Chem.*, **23**, 208 (1884); M. Lefeldt, *Pharm. Ztg.*, **49**, 146 (1904); C. Winkler, *Praktische Übungen in der Massanalyse*, 3rd ed., Leipzig 1902, p. 69.

[111] W. D. Treadwell and H. Johner, *Helv. Chim. Acta*, **7**, 533 (1924). See also K. O. Schmitt, *Z. anal. Chem.*, **71**, 273 (1927).

The sublimate is rapidly transferred to a well-stoppered weighing bottle, again heated to 100° in an oven and finally cooled over calcium chloride in an evacuated desiccator. Yet the anhydrous product is so hygroscopic that it can hardly be recommended as a standard substance.

Winkler[110] purifies oxalic acid by dissolving 550 g. in an equal weight of boiling 14% hydrochloric acid (sp. gr. 1.07) and cooling the mixture while stirring. The crystals are filtered on a funnel plugged lightly with glass wool and are washed several times with more acid, then are redissolved in fresh boiling acid and crystallized again in the same way. The product is dissolved in hot water and allowed to cool and crystallize, this process being repeated and the crystals washed with water each time until they are free from chloride. At this point Winkler dried the acid and converted it to the anhydrous form. It is better to dry to constant weight over deliquescent calcium chloride, though some difficulty is involved in obtaining the crystals free from occluded or adsorbed water. The large crystals, which otherwise are pure, may contain several tenths of a per cent of occluded water according to Hill and Smith.[112] If they are finely pulverized and dried in a desiccator containing a mixture of crystalline and anhydrous oxalic acid, they are said to reach exactly the composition $H_2C_2O_4 \cdot 2H_2O$, though Schoorl doubted this. Hill and Smith found the desired state to be attained more rapidly by passing over the powdered crystals a stream of air first dried in a large flask containing anhydrous and hydrated oxalic acid.[113] Treadwell[111] recommended the same method.

According to Schoorl[114] the vacuole water can be completely removed by first placing the dihydrate in a desiccator over calcium chloride or by allowing it to effloresce at 60° C. The dried material is then permitted to take up water by standing in the air or in a desiccator containing solid sodium bromide in contact with its saturated solution (relative humidity 60%). During dehydration the crystals fall to a very fine powder and during regeneration of the dihydrate no opportunity exists for the inclusion of excess moisture.

Tests for Purity—Nonvolatile Matter: Not more than 1 mg. of residue (0.01%) should be left after heating 10 g. of oxalic acid in a platinum crucible.

Chloride: A solution of 0.5 g. oxalic acid in 5 ml. water and 2 ml. 50% nitric acid (chloride-free) should show no turbidity or opalescence when tested with silver nitrate. Sensitivity 0.001%.

Ammonium Salts and Nitrates: Place 0.5 g. oxalic acid and 10 ml. of 4 N sodium hydroxide solution in a 25 ml. flask and stopper with a cork through which a small tube extends. In the tube place a small piece of moist red litmus paper. Heat the flask for 15 minutes on the water bath; the paper should not turn blue within this time. Sensitivity 0.001% NH_4^+. If no ammonia is indicated, add to the flask 100 mg. of zinc-iron powder and warm for 15 minutes longer. The presence of about 0.001% NO_3^- will liberate enough ammonia to turn litmus blue. The two tests may be combined if desirable. A blank should be run on the reagents in case either test is positive.[115]

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[112] A. E. Hill and T. M. Smith, *J. Am. Chem. Soc.*, **44**, 546 (1922).

[113] According to G. P. Baxter and J. E. Lansing, *ibid.*, **42**, 419 (1920), a mixture of anhydrous and crystallized oxalic acid shows a water vapor pressure of 1.15 mm. at 15°C. and of 2.65 mm. at 25°. G. P. Baxter and W. C. Cooper, Jr., *ibid.*, **46**, 924 (1924), confirmed the 25° result closely with a value of 2.69 mm. T. W. Richards, *Proc. Am. Acad. Arts Sci.*, **33**, 26 (1897), found a vapor pressure of at least 15 mm. over a saturated solution of oxalic acid at 22°C.

[114] N. Schoorl, *Chem. Weekblad*, **25**, 73 (1928).

Water:[114] 10 g. of the powdered oxalic acid should not lose more than 1 mg. after being kept in a desiccator filled with deliquescent calcium chloride crystals.

Insoluble Matter: The solution of 1 g. of acid in 10 ml. of water should be clear.

Organic Matter: The test is carried out in the same way as for sodium oxalate (p. 76), using 1 g. of oxalic acid and 10 ml. of pure sulfuric acid.

Sulfate: A mixture of 0.25 g. of the acid with a drop of 0.1 N sodium hydroxide solution in a platinum crucible is dried on the water bath, then heated from 160–200°C. until all of the oxalic acid is volatilized. If the temperature exceeds 200° much sulfate may be lost; a controlled oven or a Stock-Stähler block should be used. The residue is taken up in a little water, acidified with a few drops of 4 N acetic acid, and filtered, if necessary, then tested with barium chloride solution. No turbidity should appear. Sensitivity 0.004% $SO_4^=$.

Standardization of Alkalies against Oxalic Acid: The second ionization constant of oxalic acid is relatively small (about 5×10^{-5}) so that an indicator like phenolphthalein or thymol blue must be employed. It is possible, however, to titrate to methyl orange or methyl yellow if an excess of calcium chloride is added. In the presence of the latter, calcium oxalate is precipitated and in effect one titrates hydrochloric acid:[116]

$$H_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 + 2HCl$$

Procedure with Phenolphthalein as Indicator: Since phenolphthalein is sensitive to carbonic acid, the water used for dissolving the oxalic acid must be free from carbon dioxide. Ordinary distilled water contains too much of this and should first be boiled or aerated as described on p. 71. No other difficulty is usually encountered. The weighed amount of oxalic acid is dissolved in water and titrated with alkali to a rose color with phenolphthalein. If the color fades after the end-point, either the alkali contained carbonate or some carbon dioxide was present in the water.

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[115] The nitrate reactions with brucine–sulfuric acid and diphenylamine–sulfuric acid (Tillmans' test) are subject to interference by oxalic acid. One may, however, carry out the diphenylamine reaction as a ring test by dissolving 0.2 g. oxalic acid in 2 ml. of water with one drop of 4 N hydrochloric acid and carefully pouring down one side of the tube a 1% solution of diphenylamine in sulfuric acid. No blue ring should form; sensitivity 0.002% NO_3^-.

[116] G. Bruhns, *Z. anal. Chem.*, **45**, 575 (1906), **55**, 23, 321 (1916); *Chem.-Ztg.*, **41**, 189 (1917); *Centr. Zuckerind.*, **1906**, No. 2.

In standardizing barium hydroxide against oxalic acid a dense crystalline precipitate of barium oxalate separates during the titration. The crystals are not pure but enclose some oxalic acid or bioxalate; on this account the red color of phenolphthalein appears too soon. If the suspension is heated at this point it again becomes colorless, but on cooling and completing the titration the result may still be about 0.35% too low. Better values, even equal to the theoretical, according to Schmitt,[117] are obtained by boiling the oxalic acid solution during titration. Kolthoff and Sandell,[118] however, found that under these conditions the deviation still amounts to about 0.1%. Benzoic acid and potassium biphthalate are better suited as primary substances for the standardization of barium hydroxide.

Procedure with Methyl Yellow or Methyl Orange: The weighed amount of oxalic acid is titrated with alkali until the acid is nearly all neutralized, then 10 ml. of a neutral 20% solution of calcium chloride hexahydrate are added per 100 ml. of solution and titration is continued to the water color of the indicator (methyl yellow or methyl orange titer). The titer to phenolphthalein may also be found by continuing the titration immediately. There should not be more than 0.1 ml. difference between the two if the solutions are carbonate-free.

The calcium chloride solution should first be tested for neutrality; 25 ml. portions of the 20% solution should give an intermediate color with methyl yellow after addition of one drop of 0.1 N acid and a red color with phenolphthalein after addition of one drop of 0.1 N alkali.

Note: One should not add the calcium chloride until most of the oxalic acid has been neutralized, since oxalic acid or bioxalate is coprecipitated with calcium oxalate. Schmitt[119] in particular called attention to this source of error. If the approximate titer of the alkali is unknown it should first be estimated in a preliminary test, so that the acid may be almost completely neutralized before addition of calcium chloride in the final standardization.

Procedure with Magnesium Chloride: According to studies of Bruhns[116] the titration of oxalic acid may also be carried out sharply to methyl yellow in the presence of magnesium salts, even though no immediate precipitation of magnesium oxalate occurs. Magnesium oxalate, though it has a low solubility in water (about 1:1500), remains for a long time in supersaturated solution; moreover, it forms complex magnesium oxalate cations with excess magnesium ions. For this reason an excess of magnesium chloride is to be recommended in the titration. The magnesium chloride solution is tested for neutrality in the same way as described above for calcium chloride, but because of the greater excess required the test is made on 50 ml. of the solution rather than on 20 ml.

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[117] K. O. Schmitt, *Z. anal. Chem.*, **71**, 284 (1927).

[118] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **3**, 115 (1931).

[119] K. O. Schmitt, *Z. anal. Chem.*, **71**, 273 (1927).

In the standardization one takes 30 ml. of the 20% magnesium chloride hexahydrate solution for 100 ml. of 0.1 N oxalic acid solution. The mixture is titrated with alkali to the water color of methyl yellow. Although the end-point is not as sharp as that in a titration of hydrochloric acid, it can be recognized with sufficient accuracy if a comparison solution is used. The titration may also be continued to a phenolphthalein end-point shown by a deviation from the water color of methyl yellow. The accuracy is to within 0.2–0.3%.

Stability of Oxalic Acid Solutions: Pure 0.1 N solutions of oxalic acid may be kept in the dark for as much as a year without change, though diluted solutions are less stable. Air oxidation is accelerated by light and by catalysts, especially by manganous salts. There may also be a spontaneous decomposition to carbon monoxide and carbon dioxide. In any case a solution should be discarded if it shows moldiness. The authors prefer to keep the solution in a clear glass bottle, painted black on the outside, and to use only a fresh solution for standardizing alkali or permanganate.

Sulfamic Acid (NH_2SO_3H or $^+H_3NSO_3^-$, equivalent weight 97.09, rational 97.03): In the older literature sulfamic acid was repeatedly recommended as a primary standard for bases. Reviews of the literature have been given by Cupery[120] and by Butler, Smith, and Audrieth.[121] The compound is a strong acid in aqueous solution. Although hydrolysis slowly takes place in solution this does not change the acid titer.

$$NH_2SO_3H + H_2O \rightarrow NH_4HSO_4$$

Sulfamic acid melts with decomposition at 205°C. and on this account the crystals cannot be fused for removal of occluded water, being inferior to benzoic acid in this respect. Butler, Smith, and Audrieth purify the technical product by dissolving 125 g. in 300 ml. of water preheated to 70°. The solution is filtered three times with consequent lowering of the temperature and each time the material which crystallizes is discarded. The final filtrate is cooled rapidly in an ice–salt mixture and is allowed to stand for 20 minutes. The crystals are filtered out by suction and are washed first with a small quantity of ice water, then twice with cold alcohol and finally with ether. After air drying the product is ground and stored over anhydrous magnesium perchlorate. Though the product very likely contains occluded water and ammonium sulfate, no tests for purity are given. Therefore the acid is not to be recommended as a primary substance although it may be useful as a secondary standard.

[120] M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

[121] M. J. Butler, G. F. Smith, and L. F. Audrieth, *Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938).

Potassium Acid Iodate (KHI_2O_6, equivalent weight 389.94, rational 389.85): As a primary standard, potassium acid iodate has many advantages. Since iodic acid is a strong acid it may be titrated either to methyl yellow or to phenolphthalein. The salt has a high equivalent weight, contains no water of crystallization, is not hygroscopic and may be kept indefinitely without change. It is commercially available and may easily be prepared pure in the laboratory (see below).

Potassium acid iodate was recommended as long ago as 1877 by von Than,[122] for several purposes. He purified it by crystallizing twice and found that the solutions are stable. Meineke[123] also proposed the salt as a primary standard. Wagner[124] obtained unsatisfactory results with deviations of as much as 0.3%, but it must be noted that he based his findings on comparisons with potassium dichromate.

According to Lunge[125] the titration to methyl orange comes out a little low while that to phenolphthalein gives a good result if one follows a certain specified procedure. More recently new attention has been attracted to the salt, especially for iodometric standardizations. Shaffer and Hartmann[126] and also Koenig[127] give methods for its preparation. According to studies of Kolthoff and van Berk,[128] the compound is well suited for the standardization of alkalies.

Preparation of Pure Potassium Acid Iodate (modification of Koenig's method): Dissolve 26 g. of potassium iodate in 125 ml. of boiling water and to this add a solution of 21 g. of iodic acid in 45 ml. of warm water acidified with six drops of conc. hydrochloric acid. Potassium acid iodate separates on cooling and is filtered out by suction, washed with cold water and crystallized three times from water. In recrystallizing, one uses three parts of water for one part of the salt; the mixture should be stirred continuously during each cooling. No decomposition of the salt takes place in the process.[129] The crystals may be dried at 120°C. but no higher; preparations having an effective strength of 99.97–100.00% are obtained under the proper conditions.

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[122] C. von Than, *Math. naturw. Ber. Ungarn*, **7**, 295 (1877).

[123] C. Meineke, *Chem.-Ztg.*, **19**, 2 (1895).

[124] J. Wagner, *Massanalytische Studien.* Leiner, Leipzig 1898, p. 60.

[125] G. Lunge, *Z. angew. Chem.*, **17**, 225 (1904).

[126] P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.*, **45**, 376 (1921).

[127] M. Koenig, *Chimie & industrie*, Special Number, Sept., 1925, p. 116; *Chem. Abstracts*, **20**, 348 (1926).

[128] I. M. Kolthoff and L. H. van Berk, *J. Am. Chem. Soc.*, **48**, 2799 (1926).

[129] *Cf.* P. A. Meerburg, *Chem. Weekblad*, **1**, 474 (1904).

Standardization of Alkali against Potassium Acid Iodate: A weighed amount of the salt is dissolved in water which has first been aerated (or boiled and cooled) and the solution is titrated with alkali to the water color of methyl yellow. The phenolphthalein titer may also be found by continuing the titration to the latter indicator, taking the first deviation from the water color of methyl yellow as the end-point.

Potassium Tetroxalate ($KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, equivalent weight 84.73, rational 84.69): The crystallized salt was proposed as a standard long ago by K. Kraut[130] and has been recommended by many workers[131] while others have advised against its use.[132] Schmitt[133] recommended the preparation method of Ulbricht and Meissl,[134] by which he was able to obtain a product having an effective strength of 99.94–99.98%. One starts with separate solutions of 63 g. of pure oxalic acid and 30 g. of pure potassium oxalate, each in 100 ml. of hot water. Each solution is filtered through a folded paper and while still hot the oxalate solution is added to the acid. The mixture is stirred continuously and cooled in ice water, then the crystals are collected on a Buchner funnel and washed three times with cold water. They are sucked as dry as possible and are finally placed in an evaporating dish which is kept under reduced pressure until the contents reach constant weight. The limits of water vapor pressure within which the dihydrate is stable are not given.

Potassium Acid Oxalate (KHC_2O_4, equivalent weight 128.12, rational 128.08): This salt has been mentioned as a standard substance by Osaka and Ando[135]; it has the advantage of crystallizing without water of hydration. Unfortunately the salt cannot be recrystallized directly, however, for below 40°C, the crystals separating from a saturated solution contain the tetroxalate. The recrystallization must be made from a solution containing about 0.073 mole of oxalic acid and 0.11 mole of potassium oxalate per liter, and the temperature of this must be kept above 15° since at lower temperatures a salt containing water of crystallization is formed.

For the preparation of the salt equimolecular quantities of oxalic acid (dihydrate) and potassium oxalate (monohydrate) are mixed, and in addition 8 g. of the acid and 16 g. of the oxalate are taken for every 100 g.

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[130] *Cf.* W. Fresenius, *Z. anal. Chem.*, **26**, 629 (1887).

[131] R. Ulbricht and E. Meissl, *ibid.*, **26**, 350 (1887). C. Meineke, *Chem.-Ztg.*, **19**, 6 (1895). J. Wagner, *Proceedings of the Fifth International Congress for Applied Chemistry*, Berlin 1903. O. Kühling, *Z. angew. Chem.*, **16**, 1030 (1903); *Chem.-Ztg.*, **28**, 596, 612, 752 (1904).

[132] F. C. Wells, *J. Anal. Appl. Chem.*, **6**, 191 (1892); B. C. Hinman, *ibid.*, **6**, 435 (1892); A. Dupré, Jr., and A. v. Kupfer, *Z. angew. Chem.*, **15**, 352 (1902); G. Lunge, *ibid.*, **17**, 227 (1904).

[133] K. O. Schmitt, *Z. anal. Chem.*, **71**, 277 (1927).

[134] R. Ulbricht and E. Meissl, *Pharm. Zentralhalle*, **6**, 198 (1885).

[135] Y. Osaka and K. Ando, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **4**, 371 (1921); *Chem. Abstracts*, **15**, 1472 (1921); **16**, 3825 (1922).

portion of water used in the recrystallization. The mixture is dissolved by heating to 60°C. and the anhydrous potassium acid oxalate is crystallized out as the solution cools to 25°. The crystals are washed three or four times with water at 50° and allowed to dry in the air. A thorough testing, especially for occluded water, is needed.

Adipic Acid ($H_2C_6H_8O_4$, equivalent weight 73.07, rational 73.00): Adipic acid was recommended as a standard by van Voorst.[136] The pure acid (m. p. 152.05°C.) is obtained by recrystallizing twice from a fivefold quantity of water and drying at 130°. For the standardization one dissolves a weighed amount of the acid in hot water and titrates with alkali to phenolphthalein.

Salicylic Acid ($HC_7H_5O_3$, equivalent weight 138.12, rational 138.06): Sublimed salicyclic acid was suggested as a standard substance by Škramovský.[137] From his results it appears that the titrations with alkali average about 0.1% greater than titrations against benzoic or oxalic acid. Better agreement would be desirable.

Furoic Acid ($HC_5H_3O_3$, equivalent weight 112.08, rational 112.04): Kellog and Kellog[138] purify technical acid by sublimation and obtain a product melting at 131°C. It is very slightly hygroscopic, showing about 0.04% moisture after long exposure to air. This can be removed by fusing in a platinum dish at a temperature of not more than 142° and cooling in a desiccator. Standardizations of alkali are performed by dissolving weighed amounts of the acid in 25–50 ml. portions of carbon dioxide-free water and titrating to phenolphthalein. Results in excellent agreement with those found using Bureau of Standards benzoic acid and potassium acid phthalate were obtained by Kellog and Kellog.

Pseudocumene Sulfonic Acid ($C_9H_{11}SO_3H \cdot 2H_2O$, equivalent weight 236.31, rational 236.16): According to Tishchenko[139] pseudocumene sulfonic acid crystallizes with two molecules of water and the dihydrate has a very small vapor pressure. Since the compound behaves as a strong acid it is suggested for the standardization of alkalies.

Borax (see p. 86): Borax is less suited as a standard for bases than for acids. It may be titrated using phenolphthalein as indicator if one adds a polyhydric alcohol to convert the boric acid into a stronger complex acid. Mannitol or invert sugar is usually employed; practical details are given in Chapter IV, pp. 115, 119.

Hydrazine Sulfate ($N_2H_4 \cdot H_2SO_4$, equivalent weight 65.06, rational 65.02): Hydrazine sulfate may be obtained pure and anhydrous by recrystallization from water and drying at 140°C. It can serve as a standard for iodometry as well as alkalimetry.[140] Since the second ionization constant of hydrazine is very small, about 3×10^{-13}, the solution of the normal salt reacts strongly acid. A solution of the basic salt reacts slightly acid (p_H about 5) because the first ionization constant has a relatively small value, about 3×10^{-6}. On this account the end-point is sharpest if methyl red is used as indicator in the titration with alkali. Methyl yellow is also suitable and carbonic acid then has no disturbing effect. Phenolphthalein may not be used in the standardization.

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[136] F. T. van Voorst, *Chem. Weekblad*, **25**, 22 (1928).

[137] S. Škramovský, *Collection Czechoslov. Chem. Commun.*, **5**, 143 (1933). I. G. Murgulescu and V. Alexa, *Z. anal. Chem.*, **125**, 260 (1943), prefer to use *o*-chlorobenzoic acid, which is a stronger acid than salicylic.

[138] H. B. Kellog and A. M. Kellog, *Ind. Eng. Chem., Anal. Ed.*, **6**, 251 (1934).

[139] D. Tishchenko, *Bull. soc. chim.*, **53**, 1423 (1933).

Cadmium Sulfate ($CdSO_4 \cdot \frac{8}{3}H_2O$, equivalent weight 123.26, rational 123.21): Ashley and Hulett[141] electrolyze a solution of pure cadmium sulfate, using a mercury cathode and platinum wire anode, and obtain in this way an equivalent quantity of sulfuric acid:

$$CdSO_4 + H_2O \rightarrow Cd + \tfrac{1}{2}O_2 + H_2SO_4$$

The pure cadmium sulfate crystals are obtained by very slow (spontaneous) evaporation of a filtered concentrated solution of the C.P. salt in water. Since the crystallization process requires several weeks and the yield of usable material is small, it is best to start with a large quantity. Only the water-clear crystals are used; the cloudy ones, which may contain occluded water, are redissolved for subsequent crystallizations. The clear crystals are wiped with filter paper and stored in an atmosphere of about 70% relative humidity, as maintained in a desiccator containing a paste of sodium chloride and water. It would be worthwhile to know whether Schoorl's method of drying and then rehydrating the crystals (p. 40) could be applied in place of the above process.

Ashley and Hulett found that a sodium hydroxide solution standardized against the sulfuric acid liberated by their procedure showed a normality agreeing to within 0.04% of that determined by either of three other methods (titration of benzoic acid, potassium acid phthalate, and constant-boiling hydrochloric acid). The procedure is of scientific interest in that it furnishes an independent method of preparing standard sulfuric acid solutions. Since practical applications are likely to be infrequent, however, details are not included here.

Other Substances: Various compounds have been suggested as standards but for one reason or another have not been widely accepted. For the sake of completeness some of these are listed below. Details concerning their preparation and use may be found in the references cited.

Silver Nitrate: Feigl and Tamchyna[142] observed that a mixture of silver nitrate and mercuric cyanide gives a clear solution at a p_H of 4.2. Upon adding alkali, silver cyanide precipitates and as soon as all of the silver nitrate is consumed the solution becomes basic to methyl red or phenolphthalein. According to Feigl and Tamchyna the reaction may be used for the standardization of alkaline solutions. (Concerning the purification and testing of silver nitrate see p. 253). The utility of this procedure for standardizing alkalies has not yet been tested with sufficient accuracy.

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[140] I. M. Kolthoff, *J. Am. Chem. Soc.*, **46**, 2009 (1924); R. Stollé, *J. prakt. Chem.*, **66**, 332 (1902); F. Sommer and K. Weise, *Z. anorg. Chem.*, **94**, 51 (1916); E. Cattalain, *J. pharm. chim.*, **2**, 387 (1925).

[141] S. E. Q. Ashley and G. A. Hulett, *J. Am. Chem. Soc.*, **56**, 1275 (1934).

[142] F. Feigl and J. Tamchyna, *Ber.*, **B62**, 1897 (1929).

Organic Acids: Succinic acid has long been known as a standard[143]; succinic anhydride and malonic acid were suggested by Phelps and Weed.[144] The acids are difficult to prepare in analytically pure condition since they easily form anhydrides on drying. Moreover, organic impurities are likely to be present. The latter difficulty is also encountered with picric acid, the use of which was proposed by Sander.[145]

Acid Salts: Potassium dichromate was suggested as a standard by Richter.[146] To the advantage that it may also be used in oxidimetry is opposed the disadvantage that the titration with alkali is not sharp (see p. 147). H. Bornträger[147] proposed the use of potassium acid tartrate in standardizing alkalies; others[148] have also recommended this compound. Its solubility in water is rather low and there may also be some difficulty in obtaining a pure preparation.

Salts of Weak Bases and Strong Acids: Arndt and Nachtwey[149] recommend pyridine perchlorate as a standard. The sulfates of aniline, *o*-chloroaniline, *p*-anisidine and *p*-toluidine have been studied by Strasser,[150] who prepared them in general by dissolving the free aromatic amines in alcohol and precipitating with alcoholic sulfuric acid. The precipitated sulfates are washed with alcohol or ether and dried over calcium chloride or sulfuric acid. The salts may be dissolved in water and titrated directly with alkali, using phenolphthalein or thymolphthalein as indicator. As yet these compounds have not been tested sufficiently as standards to establish their value.

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[143] *Cf.* E. Peterson, *Z. angew. Chem.*, **13**, 688 (1900).

[144] I. K. Phelps and L. H. Weed, *Am. J. Sci.*, **26**, 138 (1908); *Z. anorg. Chem.*, **59**, 114 (1908). See also I. K. Phelps and J. L. Hubbard, *Am. J. Sci.*, **23**, 211 (1907); *Z. anorg. Chem.*, **53**, 361 (1907).

[145] A. Sander, *Z. angew. Chem.*, **27**, 192 (1914); *cf.* O. Pfeiffer, *ibid.*, **27**, 383 (1914).

[146] M. Richter, *Z. anal. Chem.*, **21**, 205 (1882). See also G. Bruhns, *J. prakt. Chem.*, **93**, 73 (1916).

[147] H. Bornträger, *Chem.-Ztg.*, **5**, 519 (1881); **14**, 1206 (1890).

[148] A. Bornträger, *Z. anal. Chem.*, **25**, 333 (1886), **31**, 43 (1892), **33**, 713 (1894). G. Favrel, *Ann. chim. anal. chim. appl.*, **9**, 161 (1927).

[149] F. Arndt and P. Nachtwey, *Ber.*, **B59**, 448 (1926).

[150] E. Strasser, *Z. anal. Chem.*, **82**, 114 (1930).

CHAPTER IV

ACID-BASE REACTIONS

1. Titration of Strong Acids with Strong Bases and Vice Versa.—From the discussions that have already been presented on this subject (Vol. I, pp. 49, 90, 146; Vol. II, p. 62), one finds that in dealing with normal solutions any indicator which changes at a p_H between 3 and 11 may be employed. In a titration with 0.1 N solution the volume of reagent required to produce an equal change in p_H is greater and the end-point is less sharp; an indicator changing between 4 and 10 should be chosen if the titration error is not to exceed 0.2%. The range is limited still more closely, from 5 to 9, in titrations involving 0.01 N solutions.

The following titrations furnish instructive laboratory experiments: 0.1 N and 0.01 N solutions of acid and alkali are prepared by diluting 1 N hydrochloric acid and carbonate-free 1 N sodium hydroxide with pure water, and 25 ml. of each acid solution is titrated with the corresponding alkali in the presence of the indicators listed in the table. In the absence of carbon dioxide the results obtained are similar to those shown below.

Indicator	Color at End-Point	Ml. Alkali Consumed by 25 ml. Acid		
		1 N	*0.1 N*	*0.01 N*
Methyl yellow	Water-color	25.00	24.95	24.6
Methyl red	Yellow (p_T = 6)	25.00	25.00	25.00
Phenol red	Yellow to red	25.00	25.00	25.00
Phenolphthalein	Pink	25.00	25.02	25.10

The difference between the methyl yellow and phenolphthalein end-points amounts to 2% with the 0.01 N solutions. If the titration is carried out in the reverse direction (starting with 25 ml. of base), one finds:

(See table, p. 106)

Indicator	Color at End-Point	Ml. Acid Consumed by 25 ml. Alkali		
		1 N	*0.1 N*	*0.01 N*
Phenolphthalein	Colorless	25.00	25.00	25.00
Phenol red	Red to yellow	25.00	25.00	25.00
Methyl red	Orange ($p_T = 5$)	25.00	25.00	25.03
Methyl yellow	First change from water-color ($p_T = 4$)	25.00	25.05	25.50

All these values are somewhat idealized, since in practice the base always contains a little carbonate and during titration a little more is taken up from the air, yet the difference between the methyl yellow and phenolphthalein end-points need not be greater than 0.4% in the titration with 0.1 N solution. The interference of carbon dioxide may be eliminated by boiling the solution for five minutes after it has been brought to the methyl yellow end-point, then completing the titration after cooling. The difference between the methyl yellow and phenolphthalein end-points under these conditions should not exceed 0.2%. From the ratios obtained in such studies one derives a good idea of the titration error.

The above measurements refer to room temperature. At the boiling point the conditions are changed as follows:

(*a*) The change of hydrogen-ion concentration at the equivalence-point becomes less pronounced, since the value of K_w at 100°C. is 100 times greater than at room temperature.

(*b*) The sensitivity of the indicator toward hydrogen or hydroxyl ions may be changed. As was seen in Vol. I (p. 95), at higher temperatures indicators of basic character become less sensitive for hydrogen ions, and those of acid nature less sensitive for hydroxyl ions. Thus the basic indicators methyl yellow and methyl orange fail to give a sharp change in titrations with 0.1 N solution at higher temperatures, while the acid indicator bromophenol blue is still useful although it has nearly the same transition interval as the others at room temperature. Conversely, the sensitivity of phenolphthalein toward hydroxyl ions diminishes as the temperature is raised.

The behavior of indicators in titrations with liquids containing a small amount of carbon dioxide, as is usually the case, should be mentioned here. Methyl orange is scarcely affected by a trace of carbonic acid and its color change is therefore independent of the carbonic acid content of the solution. On the contrary, phenolphthalein allows carbonic acid to be titrated as a monobasic acid (*cf.* p. 133). For this reason the rose color which first appears with phenolphthalein and alkali fades out to colorless as fast as carbonic acid, in the form of its anhydride CO_2, dissolves and undergoes the reaction:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

or

$$CO_2 + OH^- \rightleftarrows HCO_3^-$$

either of which proceeds with measurable velocity. The fading of the phenolphthalein color should therefore be ascribed to the behavior of the carbonic acid rather than to any peculiarity of the indicator. Thymol blue, cresol red and phenol red exhibit the same fading under similar circumstances.

The problem of titrating very dilute acid solutions with alkali, or vice versa, frequently arises. In order to eliminate carbon dioxide interference one may titrate at the boiling point with the use of phenol red, cresol red, bromothymol blue, or even methyl red as indicator. In the titration of 0.005 N hydrochloric acid, for example, alkali is first added at room temperature until the color of methyl red begins to change, then the solution is boiled and the titration continued to the pure yellow color of this indicator. An accuracy of 0.2% is possible. By titrating 0.001 N acid to the orange intermediate color of phenol red at boiling, results accurate to within 0.5% may be obtained. In the reverse titration of base with acid, the end-points are taken at the first deviation from the yellow color of methyl red, or at the pure yellow color of phenol red (at boiling). In these determinations one must of course use resistant glassware to avoid the introduction of alkali from the apparatus.

If a precipitate forms during a neutralization titration, the results are subject to another error, that due to occlusion of acid or base by the precipitate. A case of this kind, the direct or reverse titration of barium hydroxide with sulfuric acid, was investigated by Kolthoff and Sandell.[1]

In the titration of sulfuric acid with barium hydroxide at room temperature, the first end-point with methyl red or phenolphthalein appears too soon and is not permanent. If the solution is boiled in the presence of the precipitate at this point, a further addition of barium hydroxide is necessary to produce the alkaline color. If this color does not remain upon 15–30 seconds of heating, the mixture is boiled for five minutes longer and the titration is completed after cooling. Even under these conditions the determination is not more accurate than to 0.1 or 0.2% (small but unavoidable inclusions of acid). By allowing the barium solution to flow into the hot acid while stirring, up to about 0.6% of base may be occluded. In the titration of barium hydroxide with sulfuric acid the base is strongly adsorbed and enclosed; deviations of 1–3% from the theoretical may be observed. However, values accurate to 0.2% or better are possible if one first adds the barium hydroxide to an excess of neutral potassium sulfate at room temperature, then titrates with acid in slight excess (1 ml.), boils for several minutes, cools, and titrates back with barium hydroxide to the phenolphthalein or methyl red end-point.

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[1] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 3, 115 (1931).

In general, direct or reverse titrations of barium hydroxide with sulfuric acid are not to be recommended for accurate work.

Assay of Caustic Alkalies: Since caustic soda and potash are available in various grades of purity and even the purest grades contain carbonate due to superficial absorption of moisture and carbon dioxide, it is of practical importance to be able to determine the hydroxide in the presence of carbonate. As has already been seen, methyl yellow and bromophenol blue are not sensitive to carbonic acid; therefore the sum of the alkali hydroxide and carbonate (total alkalinity) can be found by an acid titration with one of these indicators. The hydroxide alone may be determined, preferably by Winkler's method (*a*), or if the amount of carbonate is small, by Warder's method (*b*).

(*a*) *Procedure for Winkler's Method:* The rapidly weighed sample is dissolved in carbon dioxide-free water and diluted to known volume in a volumetric flask. To an aliquot portion a sufficient excess of neutral 10% barium chloride solution is added so that after precipitation of the carbonate the solution will be at least 0.1 N in barium ions, then the suspension is titrated with acid to the phenolphthalein end-point while being stirred constantly. The difference between this titration and that found for the total alkalinity on another aliquot part represents the carbonate.

Notes: (1) A suspension of pure barium carbonate reacts appreciably alkaline to phenolphthalein, but the solubility is so strongly repressed by an excess of barium ions that under these conditions the mixture behaves as though neutral.

(2) According to Sörensen and Andersen,[2] a solution of sodium carbonate treated with excess barium chloride in the cold reacts appreciably alkaline to phenolphthalein because a little acid salt (bicarbonate) is coprecipitated. By precipitation from hot solution pure barium carbonate is formed, but in the

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[2] S. P. L. Sörensen and A. C. Andersen, *Z. anal. Chem.*, **45**, 220 (1906); **47**, 279 (1908). See also M. Le Blanc and K. Novotny, *Z. anorg. allgem. Chem.*, **51**, 181 (1906); **53**, 344 (1907).

presence of alkali hydroxide the precipitate occludes basic salts, the more so the higher is the hydroxyl-ion concentration. Therefore Winkler's method gives good results, according to Sörensen and Andersen, only if the precipitation is made from a warm solution containing practically nothing but normal carbonate. Before the solution is warmed the alkali hydroxide should be approximately neutralized with an amount of hydrochloric acid as determined in a preliminary test.

For the analysis of commercial alkali, which generally contains only small amounts of carbonate, one may according to the authors' experience follow Winkler's procedure without committing a significant error. Furthermore, if much more carbonate than hydroxide is present the precipitation may be made cold. Thus 5 ml. of 0.1 N carbonate-free sodium hydroxide in 20 ml. of water required 4.98 ml. of 0.1 N hydrochloric acid to phenolphthalein, while the same amount of alkali with 25 ml. of 10% barium chloride solution took 5.00 ml. A mixture of 5 ml. of 0.1 N alkali with 10 ml. of pure 5% sodium carbonate solution after precipitation in the cold with 25 ml. of 10% barium chloride required 5.00–5.05 ml. of 0.1 N acid.

(3) If larger quantities of carbonate are present too little alkali is found, according to Lindner,[3] because hydroxide is carried down with the barium carbonate. Lindner finds precipitation at a higher temperature to be ineffective and recommends instead cooling with ice, but in either case the solution should be diluted to less than 0.5 N. Even with greater carbonate content the errors remain small when the titrations are performed at room temperature, and the deviations are still lower if after the first titration a second determination is made with the approximately correct amount of acid added before precipitation. One should always bear in mind that with silicate-containing samples a part of the silicic acid will accompany the carbonate as barium silicate; too high a result for the carbonate will then be obtained. Under these conditions, and also when the carbonate content is very small, a direct carbonic acid determination is to be recommended.

(4) The investigation of Poethke and Manicke[4] confirmed that the addition of barium chloride and titration at room temperature are suitable. Still better results were obtained by letting the hydroxide–carbonate mixture flow from a moving pipette into a barium chloride solution of such strength that the barium salt concentration after precipitation was about 0.1 N.

(5) According to Partridge and Schroeder[5] the Winkler method does not always yield reliable results for the carbonate determination in the presence of free alkali in boiler waters. Sulfate in particular causes the values to be too high. On the other hand, Straub[6] obtained good results, at least in the absence of silicic acid.

(*b*) *Procedure for Warder's Method:*[7] To an aliquot part of the solution one adds phenolphthalein and titrates with acid to the point of decolorization, meanwhile swirling the solution. This titration of *a* ml. corresponds to the hydroxide plus half of the carbonate. Then further acid is added until the methyl yellow end-point is reached. If the volume of additional acid is *b* ml., then $(a - b)$ ml. of acid is equivalent to the hydroxide originally present.

[3] J. Lindner, *Z. anal. Chem.*, **72**, 135 (1927); **78**, 188 (1929).

[4] W. Poethke and P. Manicke, *Z. anal. Chem.*, **79**, 241 (1929).

[5] E. P. Partridge and W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **4**, 271 (1932).

[6] G. Straub, *Ind. Eng. Chem., Anal. Ed.*, **4**, 290 (1932).

[7] R. B. Warder, *Am. Chem. J.*, **3**, 55, 232 (1881); *Chem. News*, **43**, 228 (1881).

Notes: (1) The titration of carbonate to bicarbonate with phenolphthalein does not show a sharp end-point (see p. 132). Yet if only a small amount of carbonate is present the titration error in the determination of alkali hydroxide may be neglected.[8]

(2) A critical comparison of Warder's method with Winkler's was contributed by Suchier.[9] In case the sodium hydroxide content exceeds 97% the average deviations with Winkler's method range from +0.1 to −0.15%, and with Warder's from −0.2 to −0.4%. According to Suchier, therefore, the Winkler procedure is slightly superior in accuracy.

(3) Benedetti-Pichler and co-workers[10] made an extensive study of Warder's method. In order to avoid loss or gain of carbon dioxide they recommend performing the titration in a closed system, using for this purpose a 250 ml. volumetric flask with long narrow neck and glass or cork stopper.[11] A measured volume of carbonate solution is introduced into the flask, 0.1 ml. of 1% phenolphthalein is added and the titration is begun with standard hydrochloric acid. At the start the acid is added in relatively large portions and after every addition the flask is stoppered and shaken vigorously for about 20 seconds. When the color of the titrated solution brightens to pink, the acid is added in 0.2 ml. portions, then in single drops, and eventually in fractions of drops. Simultaneously the time of shaking is lengthened the nearer the end-point is approached, so that finally one shakes for a full minute and then waits another minute before comparing with the color standard. The latter contains the same amounts of pure sodium bicarbonate, sodium chloride, and indicator and is of the same volume as the unknown at the end-point. The comparison solution is kept in a closed flask and is also shaken occasionally. In the titration of pure carbonate the authors claim a reproducibility of 0.15–0.2%. The precision becomes less with increasing amounts of bicarbonate in the carbonate solution.

Determination of Free Acids or Alkalies in the Presence of Hydrolyzable Substances: Special methods are needed for the titration of free acidity or alkalinity in the presence of easily hydrolyzed salts or of reagents which interfere with indicators. Some cases typical of those that may be encountered in industrial analysis are noted below.

Free Alkali in Hypochlorite, etc.: According to Rupp and Lewy[12] the free alkali or sodium carbonate in hypohalite solutions may be titrated after reduction with neutral hydrogen peroxide:

$$NaClO + H_2O_2 \rightarrow NaCl + H_2O + O_2$$

Free Alkali in Sodium Stannate Solution: The hydrolysis of an alkali stannate may be expressed by the equation:

$$Sn(OH)_6^{=} + 2H_2O \rightarrow Sn(OH)_4 + 2H_2O + 2OH^-$$

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[8] G. Lunge, *Z. angew. Chem.*, **11**, 41 (1897).

[9] A. Suchier, *Z. angew. Chem.*, **44**, 534 (1931).

[10] A. A. Benedetti-Pichler, M. Cefola, and B. Waldman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 327 (1939).

[11] See J. Tillmans and O. Heublein, *Z. angew. Chem.*, **24**, 874 (1911).

[12] R. Rupp and F. Lewy, *Z. anal. Chem.*, **73**, 283 (1928).

Reiff and Toussaint[13] eliminate the hydrolysis by adding a 10% solution of catechol, with which stannate forms a neutral complex:

$$Sn(OH)_6^{=} + 3C_6H_4(OH)_2 \rightarrow [Sn(C_6H_4O_2)_3]^{=} + 6H_2O$$

Free alkali present in the solution can then be determined by titrating with acid to the yellow color of bromothymol blue.

Free Acid in Aluminum or Ferric Salt Solutions: These solutions are normally acid in reaction and the p_H changes on addition of small amounts of acid or base are very slight, so that direct titration to the p_H of the pure salt solution is not satisfactory (*cf.* p. 184). Feigl and Krauss[14] by addition of excess alkali oxalate convert aluminum into a complex oxalate which reacts neutral. Any free acid originally present can then be titrated iodometrically or, according to Hahn and Hartleb,[15] with alkali to phenolphthalein. Small amounts of free acid cannot be determined accurately in this way. For example, upon treatment of 1 g. potassium alum with 30 ml. of water and 20 ml. of 20% potassium oxalate solution, the following endpoints could be obtained in titrating with 0.1 N alkali:

3.0 ml. to phenolphthalein (p_H about 8, not sharp)
1.5 ml. to phenol red (p_H about 7.6, not sharp)
0.4 ml. to green color of thymol blue
0.7 ml. to blue-green of thymol blue

Craig[16] tests aluminum salts for the presence of free acid or basic salts by adding the dissolved sample to an excess of strong potassium fluoride solution previously neutralized to phenolphthalein:

$$Al^{+++} + 6F^- \rightleftarrows AlF_6^{\equiv}$$

The complex fluoaluminate ion reacts neutral to phenolphthalein, so that any free acid may be titrated to this indicator with alkali. In case the mixture shows an alkaline reaction, a basic salt was originally present. One then adds a known excess of acid, heats, cools, and back-titrates; direct titration with acid gives erroneous results because a basic double fluoride separates.

A similar reaction can be employed in the analysis of ferric chloride solutions. The authors have found the following directions useful, provided that ferrous salts or other interfering substances are absent.

Procedure: To a 4 g. sample of the ferric chloride, dissolved in 100 ml. of water in a 250 ml. volumetric flask, add 30 g. of potassium fluoride dihydrate which has previously been dissolved in 100 ml. of water and adjusted to a faint pink color with phenolphthalein as indicator. Dilute to the mark with water, mix well, allow the precipitate to settle, and titrate a 100 ml. portion of the supernatant liquor with alkali to the same pink shade, adding enough phenolphthalein to make its concentration the same in the aliquot as in the fluoride solution.

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[13] F. Reiff and S. M. Toussaint, *Z. anal. Chem.*, 116, 404 (1939).

[14] F. Feigl and G. Krauss, *Ber.*, 58, 398 (1925).

[15] F. L. Hahn and E. Hartleb, *Z. anal. Chem.*, 71, 225 (1927).

[16] T. J. I. Craig, *J. Soc. Chem. Ind.*, 30, 184 (1911).

Free Acid in Cupric (and Ferric) Salts: Ortner[17] makes use of the complex formation between these salts and thiourea. Apparently the copper complex ion has the composition $[Cu(N_2H_4CS)_6]^{++}$ and is colorless. Ortner adds to the copper salt solution several grams of ammonium sulfate and sufficient thiourea to remove the color, then titrates the free mineral acid to methyl orange.

Complex formation between ferric iron and thiourea takes place slowly but is catalyzed by copper salts. To the rather dilute ferric solution are added about 0.25 g. copper sulfate and 3–5 g. ammonium sulfate, then the thiourea is introduced all at once, the mixture is shaken vigorously, and titrated after it becomes colorless.

2. Titration of Weak Acids with Strong Bases.—In the theoretical part (Vol. I, p. 52) the neutralization curves of weak acids are discussed, with the conclusion that in the determination of such acids an acid-sensitive indicator like phenolphthalein should be used. From the neutralization curve the sharpness of the end-point can also be predicted. In many important cases the change in hydrogen-ion concentration at the end-point is so abrupt that one can titrate to the color change of the indicator without using a reference solution. However this is not always true; the course of the p_H and hence the sharpness of the end-point depend upon the ionization constant and concentration of the acid.

The following table, prepared with the aid of considerations discussed in Volume I, enables one to tell readily the conditions under which an acid of given ionization constant can be titrated accurately with a strong base. In the table, p_T represents the p_H at the equivalence-point, and values of the p_H are given for this point and for points 0.2% before and after it in the titrations of various acids. The calculations were based on a value of 10^{-14} for K_w, which holds at average room temperatures (24°C.). Activity coefficients of the anions were considered to be 0.7 in 0.5 N salt solutions, 0.85 in 0.05 N, and unity in 0.005 N solutions. With divalent anions the coefficients would be somewhat smaller but for practical purposes would not change the results seriously.

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[17] G. Ortner, *Z. anal. Chem.*, **112,** 96 (1938).

HYDROGEN-ION CONCENTRATIONS NEAR THE EQUIVALENCE-POINT IN TITRATIONS OF WEAK ACIDS WITH STRONG BASES

Ionization Constant, K_a	Titration of 1 N Solutions			Titration of 0.1 N Solutions			Titration of 0.01 N Solutions		
	p_H 0.2% before p_T	p_T	p_H 0.2% after p_T	p_H 0.2% before p_T	p_T	p_H 0.2% after p_T	p_H 0.2% before p_T	p_T	p_H 0.2% after p_T
10^{-3}	5.5	8.3	11.0	5.6	7.8	10.0	5.70	7.35	9.0
10^{-4}	6.5	8.8	11.0	6.6	8.3	10.0	6.70	7.85	9.0
10^{-5}	7.5	9.3	11.0	7.6	8.8	10.0	7.70	8.35	9.0
10^{-6}	8.5	9.8	11.0	8.6	9.3	10.0	8.57	8.85	9.14
10^{-7}	9.5	10.3	11.0	9.56	9.8	10.13	9.25	9.35	9.46
10^{-8}	10.44	10.8	11.1	10.21	10.3	10.42	9.83	9.85	9.87
10^{-9}	11.16	11.3	11.39	10.78	10.8	10.82	10.35	10.35	10.35
10^{-10}	11.76	11.8	11.85						

Titration of 0.01 N Acids with 0.01 N Alkali: By titrating to a deviation from the water color with phenolphthalein or thymol blue as indicator, one can determine an acid of ionization constant greater than about 3×10^{-6} with an error of less than 0.2%. Weaker acids may be determined if one employs a comparison solution having the same p_H and amount of indicator as the titrated solution at the equivalence-point. If the end-point can be perceived accurately to within 0.1 p_H unit, an acid with ionization constant as low as 10^{-7} can be determined. Still weaker acids cannot be titrated accurately at this dilution.

Titration of 0.1 N Acids with 0.1 N Alkali: With thymolphthalein as indicator (p_T about 10) an acid of constant greater than 5×10^{-7} can be titrated to within 0.2%. In case one employs a comparison solution of the correct p_H, determinations of this accuracy are possible with acids having constants nearly as small as 10^{-8}. Veronal, of which $K_a = 3 \times 10^{-7}$, may be titrated quite accurately using a reference standard.

As reference solution one may select a buffer mixture whose p_H corresponds to the titration exponent.[18] In principle it is preferable to use the pure alkali salt of the acid being titrated, if such is available; its concentration should be made equal to that of the titrated solution at the equivalence-point.

Titration of 1 N Acids with 1 N Alkali: Acids with ionization constants greater than 10^{-6} may in 1 N solution be titrated accurately with phenolphthalein as indicator. If the constants lie between 10^{-6} and 3×10^{-8}, thymolphthalein may be used without a reference solution. Acids with still smaller constants show such a slight p_H change at the equivalence-point that a comparison solution is necessary; in this way an acid of ionization constant 5×10^{-10} can be titrated with accuracy approaching 0.5%. Nitramine or tropeolin O serves best as indicator. Because of the high alkalinity of the solution at the equivalence-point, a very dilute solution of sodium hydroxide may be used for comparison ($p_{OH} = 14 - p_T$), yet one must be careful to avoid the introduction of carbon dioxide from the air. A sodium carbonate solution is preferable. However, since the salt concentration at the end-point is fairly large (0.5 N) in titrations of 1 N solutions, it is still better to use for reference a solution of the sodium salt of the acid in question, thus compensating for the salt error of the indicator.

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[18] See, for example, I. M. Kolthoff, *Acid-Base Indicators*, translated by C. Rosenblum. Macmillan, New York 1936.

In this way even such weak acids as boric (K_a about 6×10^{-10}), hydrocyanic ($K_a = 7 \times 10^{-10}$) and phenol ($K_a = 2 \times 10^{-10}$) may be titrated with errors of 0.5–1%.[19] Since the conditions under which one can determine an acid of known ionization constant are obvious from the foregoing considerations, it is unnecessary to take up the various acids individually. Only a few special cases will be discussed in succeeding paragraphs.

Boric Acid: This very weak acid can be titrated directly only in about a normal solution, with tropeolin O or nitramine as indicator. With 0.05 M sodium carbonate as reference solution the error may amount to 1 or 2%.[19] In calculating the titration exponent it must be considered that boric acid behaves somewhat abnormally; its "ionization constant" rises appreciably with increasing concentration due to the formation of a stronger polyboric acid. Thus values of K_a at 18°C. have been found[20] to equal 4.6×10^{-10} in 0.1 M solution, 2.6×10^{-9} in 0.25 M, and 1.19×10^{-8} in 0.5 M. Naegeli[21] has applied his turbidity indicators to the boric acid titration. He added excess alkali and titrated back with 0.1 N acid against indicator I (page 50) to the appearance of a turbidity; the error amounted to 2 or 3%.

Schäfer and Sieverts[22] showed that the apparent ionization constant of boric acid is greatly increased by the presence of lithium, barium, strontium, and especially calcium salts. In a solution which is 5.4 N in calcium chloride the apparent constant is about 10^{-4}. Use of this fact is made in the titration of boric acid.

Procedure: To 40 ml. or less of the solution add 5 drops of 0.1% methyl red indicator and neutralize if necessary. Saturate the solution with crystalline calcium chloride hexahydrate and titrate with standard sodium hydroxide until the red color changes to orange. Add more calcium chloride, so that an excess of solid is present, and complete the titration dropwise. The color change is from red-orange to orange-yellow.

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[19] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **115**, 168 (1921). See also E. B. R. Prideaux, *ibid.*, **83**, 362 (1913).

[20] I. M. Kolthoff, *Rec. trav. chim.*, **45**, 501 (1926).

[21] K. Naegeli, *Kolloidchem. Beihefte*, **21**, 305 (1925).

[22] H. Schäfer and A. Sieverts, *Z. anorg. allgem. Chem.*, **246**, 149 (1941). See also *Z. anal. Chem.* **121**, 170 (1941).

Notes: (1) Since calcium chloride often contains traces of boric acid, a blank should be run if the amounts in question are small.
(2) The titration also gives good results in the presence of zinc salts.

Determinations of boron are generally based on the fact that boric acid reacts with polyvalent alcohols to form stronger complex acids which can be titrated sharply to phenolphthalein. The addition of neutral glycerin was early recommended by Thomson[23]; later the utility of other polyalcohols was studied. Mannitol has proved to be more suitable than glycerin; it is available in pure form, a smaller amount is necessary (0.5–0.7 g. per 10 ml.), and the color change is sharper since the boromannitol complex is a stronger acid and also because the first reddening is more easily perceptible than in the viscous glycerin solution. Investigations of Böeseken[24] have shown that invert sugar has some advantages over mannitol. Although glucose yields a weaker boric acid complex than mannitol, fructose gives one which is even stronger.

The method of Gilmour[25] for the preparation of invert sugar can be recommended. Dissolve about 3 kg. of sucrose in a liter of distilled water, best in a large tinned container, and boil for several minutes until clear. Quickly add 25 ml. of 3 N sulfuric acid and stir the mixture for half a minute, then pour in 1.5 l. of water containing 25 ml. of 3 N sodium hydroxide (carbonate-free), stir again and cool. The product will be about 4.5 l. of an approximately 55% solution of invert sugar; it should be clear and colorless.

Titration Procedure: For every 10 ml. of 0.1 N boric acid add 3–4 ml. of invert sugar solution and titrate with carbonate-free alkali to a rose color with phenolphthalein. Then add 5 ml. more of invert sugar and if the color fades titrate further, repeating the addition of sugar and alkali until the color remains.

Notes: (1) In place of phenolphthalein, Strecker and Kannappel[26] recommend α-naphtholphthalein as indicator. The change with this indicator is quite distinct (titration to green), otherwise it has no especial advantages over phenolphthalein.

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[23] R. T. Thomson, *J. Soc. Chem. Ind.*, **12**, 432 (1893).

[24] J. Böeseken and collaborators, *Rec. trav. chim.*, **30**, 392 (1911); **34**, 96 (1915); **37**, 130, 184 (1918); **40**, 553 (1921); **59**, 97 (1940); *Verhandel. Akad. Wetenschappen Amsterdam*, **29**, 368 (1920).

[25] B. Gilmour, *Analyst*, **46**, 3 (1921); **49**, 576 (1924). S. S. Dodd, *ibid.*, **55**, 23 (1930) has tested systematically the various procedures for titrating boric acid. See also M. G. Mellon and V. N. Morris, *Ind. Eng. Chem.*, **16**, 123 (1924).

[26] W. Strecker and E. Kannappel, *Z. anal. Chem.*, **61**, 378 (1922).

(2) If glycerin rather than invert sugar is used it must first be neutralized to the same indicator, since it usually contains a little free acid. For 10 ml. of 0.1 N boric acid one allows 10 ml. of glycerin.

Weatherby and Chesny[27] recommend the use of glucose instead of glycerin or mannitol. Ten times as much glucose as mannitol is needed, but it is cheaper. Either compound can readily be obtained in sufficiently pure condition.

(3) Informative studies on the theory of complex formation were published long ago by Magnanini[28] and later by Böeseken and co-workers.[24] Van Liempt[29] studied potentiometrically the neutralization curves of boric acid in the presence of glycerin or mannitol under varying conditions. For details concerning the individual processes, which have turned out to be quite complicated, the reader is referred to these papers.

(4) Since the complex acids that are formed become much less stable with rising temperature it is desirable to perform the titration at as low a temperature as possible in order to obtain a sharp color change of the indicator.

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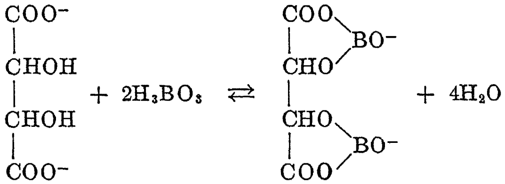

Citrate, lactate, salicylate, etc., behave similarly. If salts of these organic acids are present it is necessary to use much more mannitol, invert sugar or other polyalcohol to overcome the interference.[30]

(6) To determine boric acid in the presence of strong acids one first neutralizes the solution to the yellow color of methyl yellow or methyl orange or to an intermediate shade with methyl red. The p_H of a 0.1 N boric acid solution is about 5. For the determination in the presence of weak acids, see p. 118 as well as the titration methods of Foote and of Schäfer and Sieverts, p. 119, which are applicable when the buffering action of the weak acid is not too great.

Removal of Interfering Substances: Menzel[31] expels ammonium salts, in the analysis of ammonium borate, for example, by boiling with excess alkali. The solution is then made slightly acid and warmed to eliminate carbon dioxide, the free acid is neutralized to methyl red, and the usual titration with alkali is carried out in the presence of mannitol and phenolphthalein.

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[27] L. S. Weatherby and H. H. Chesny, *Ind. Eng. Chem.*, **18**, 820 (1926).

[28] G. Magnanini, *Z. physik. Chem.*, **6**, 58 (1890).

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[30] I. M. Kolthoff, *Rec. trav. chim.*, **45**, 607 (1926).

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Schäfer and Sieverts[32] remove zinc, nickel, ferric iron, and aluminum by precipitation with 8-hydroxyquinoline, added as a 0.25 M solution of the sodium salt. The excess of reagent is removed with magnesium chloride.

The neutral[33] or weakly acid solution to be analyzed is heated to 60°C. and treated with a *slight* excess of sodium oxinate solution (7.5 g. of 8-hydroxyquinoline dissolved in 50 ml. of 1 N sodium hydroxide and diluted to 200 ml.). The solution at this point should react alkaline to bromocresol purple. After keeping the suspension warm for 5 minutes, 5 ml. of 1 M magnesium chloride is added and heating is continued for 5 minutes longer. The precipitate is filtered off and washed with water at room temperature, and the filtrate is made just acid to methyl red; 0.5 g. of animal charcoal is added and the mixture is filtered after 5 minutes. The charcoal is washed with water and the filtrate is neutralized preparatory to titration of boric acid by the foregoing method.

Phosphate may be removed, according to Polenske,[34] by precipitation with ferric chloride and sodium hydroxide. Allen and Tankard[35] and also Shrewsbury[36] recommend the use of calcium chloride in alkaline solution. Neither of these procedures appears attractive for exact work. Schäfer and Sieverts[32] precipitate phosphate by adding silver nitrate and adjusting to p_H 5.8. After filtration and washing, the filtrate is treated with sodium chloride and the boric acid is titrated without removal of silver chloride. The same procedure serves to remove arsenate. Trivalent antimony is removed by heating the alkaline solution, slightly acidifying with hydrochloric acid, and filtering.

Larger quantities of silica are removed by adding 3 g. of ammonium chloride to 10–15 ml. of the alkaline borate–silicate solution. Silicic acid precipitates as a gel. After 5 minutes the solution is neutralized with 6 N hydrochloric acid and 10 drops are added in excess. The mixture is boiled, placed for 10 mend α-naphtholphthalein as indicator. The change with this indicator is quite distinct (titration to green), otherwise it has no especial advantages over phenolphthalein.

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[32] H. Schäfer and A. Sieverts, *Z. anal. Chem.*, **121**, 161 (1941). See also G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, **3**, 91 (1929).

[33] From their paper it is not clear how Schäfer and Sieverts neutralize solutions containing iron or aluminum before adding sodium oxinate. During neutralization to methyl red or bromocresol purple, iron and aluminum precipitate as hydrous oxides which adsorb boric acid. It would seem best to add the oxinate to a slightly acid solution. The authors have found that while the hydrous oxides adsorb appreciable amounts of boric acid from moderately strong solutions (such as would be titrated with 0.1 N alkali), the adsorption is negligible from dilute solutions (titratable with 0.01 N alkali). Thus iron and aluminum may be removed from dilute boric acid solutions by a simpler hydroxide precipitation. Boiling with pure magnesium carbonate is convenient, according to unpublished experiments of E. G. Bobalek. Incidentally it may be noted that boric acid is much more strongly coprecipitated with magnesium hydroxide than with iron or aluminum hydroxide. The possibility of loss through such a coprecipitation should be carefully avoided.

[34] E. Polenske, *Arb. Reichsgesundh.*, **17**, 564 (1900).

[35] A. H. Allen and A. R. Tankard, *Analyst*, **29**, 301 (1904).

[36] H. S. Shrewsbury, *Analyst*, **32**, 5 (1907).

(2) If glycerin rather than invert sugar is used it must first be neutralized to the same indicator, since it usually contains a little free acid. For 10 ml. of 0.1 N boric acid one allows 10 ml. of glycerin.

Weatherby and Chesny[27] recommend the use of glucose instead of glycerin or mannitol. Ten times as much glucose as mannitol is needed, but it is cheaper. Either compound can readily be obtained in sufficiently pure condition.

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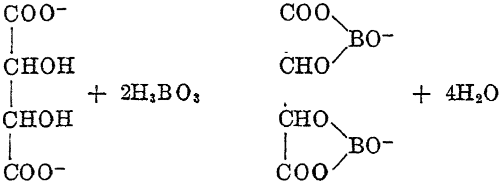

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[32] H. Schäfer and A. Sieverts, *Z. anal. Chem.*, **121**, 161 (1941). See also G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, **3**, 91 (1929).

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For the determination of boron in glass, Glaze and Finn[37] present an empirical method in which the solution obtained by fusing the sample with sodium carbonate and neutralizing with sulfuric acid is extracted with an alcohol–ether mixture. Under carefully controlled conditions a definite fraction of the boric acid enters the solvent layer and may be titrated after removal of the solvents. The original paper should be consulted for details. Fluoride interferes, but barium, zinc, iron, or lead do not, provided that chlorides are absent.

The most general method for removal of interfering elements consists in distilling boric acid as its methyl ester.[38] The sample is treated with concentrated hydrochloric acid and enough anhydrous calcium chloride to take up the water, then is distilled with methyl alcohol, and the distillate is caught in an excess of alkali. The distillate is evaporated to expel alcohol, neutralized to methyl orange with hydrochloric acid, boiled one or two minutes to liberate carbon dioxide, cooled, and titrated as above. Schulek and Vastagh[39] studied the distillation method especially with mixtures containing silicic acid. In the presence of both iron and silica they employed a double distillation. Funk and Winter[40] obtained incomplete volatilization of boron from large amounts of aluminum salts; they suggested precipitating most of the aluminum with phosphate before distilling.

An empirical method of eliminating the interference of small amounts of many metal salts, phosphate, fluoride, etc., without distillation, depends upon titrating to the same p_H both before and after the addition of mannitol or invert sugar. Foote,[41] who suggested the procedure, titrated with the aid of phenol red indicator to a p_H of 7.6, using a buffer solution for comparison; the authors prefer a mixed indicator of bromothymol blue and phenol red (p. 59) with titration to the violet color. The procedure is best adapted to the determination of small quantities of boric acid. Since the equivalence-point is passed in the first titration and not quite reached in the second, a correction factor has to be applied. With from 1–200 mg. of boric acid, alone or in the presence of sodium chloride, this factor is about 1.04. The factor increases strongly with large concentrations of calcium or magnesium salts, probably because of their effect on the ionization constant of the free acid (p. 114). For a given set of conditions one can determine the factor by titrating known mixtures of pure boric acid and the salts in question.

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[37] F. W. Glaze and A. N. Finn, *J. Research Natl. Bur. Standards*, 27, 33 (1941).

[38] *Cf.* W. H. Chapin, *J. Am. Chem. Soc.*, 30, 1691 (1908); L. V. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 2, 358 (1930).

[39] E. Schulek and G. Vastagh, *Z. anal. Chem.*, 84, 167 (1931); *ibid.*, 87, 165 (1932). See also E. T. Allen and E. G. Zies, *J. Am. Cer. Soc.*, 1, 739 (1918), for the determination of boron in glass.

[40] H. Funk and H. Winter, *Z. anorg. allgem. Chem.*, 142, 257 (1925).

[41] F. J. Foote, *Ind. Eng. Chem., Anal. Ed.*, 4, 39 (1932).

A refinement of the procedure has been contributed by Schäfer and Sieverts,[42] who found that in a 2 M solution of invert sugar (or mannitol) boric acid behaves as an intermediately strong acid and may be titrated to a p_H of 5.8. The solution, containing up to 70 mg. of boric anhydride, is first freed from any lead by precipitation as sulfate and from iron and aluminum by oxine or hydroxide separations (p. 117). It is then made weakly alkaline and evaporated to a volume of 30–40 ml. To minimize the extraction of borate from Jena (or Pyrex) glassware, Schäfer and Sieverts add a slight excess of magnesium chloride. The authors prefer to carry out the evaporation in a nickel or monel beaker. Finally the solution is acidified and boiled to expel carbon dioxide, cooled, and neutralized to a change from yellow to blue-purple with bromocresol purple as indicator. Enough invert sugar is added to make the concentration 2 M and the solution is titrated with 0.1 N carbonate-free sodium hydroxide to the same color that it had before addition of sugar. In order to work with mannitol, which is less soluble, the solution is titrated nearly to the end-point with an excess of the solid present, then is heated and cooled carefully so that it becomes supersaturated, and the titration is completed as before.

The procedure was shown to give good results in the presence of moderate amounts of zinc, nickel, cadmium, cobalt, manganese, and ammonium salts, which interfere in the classical titration to a p_H of about 8.5. Small quantities of phosphate, arsenate, and arsenite can also be tolerated.

Determination of Alkalies as Borates: Schulek and Szlatinay[43] found that the alkali salts of certain acids, such as *carbonates*, *nitrates*, *nitrites*, *halides*, *cyanides*, *sulfides*, *sulfites*, *thiosulfates*, *sulfates*, *arsenates*, and *arsenites*, can be converted into borates by mechanically mixing with a small excess of boric acid in a platinum dish and heating to dull redness. After cooling, the borate is dissolved in water and titrated with standard acid (*cf.* p. 150). Nitrates and nitrites are transformed most easily; halides require longer heating, during which some alkali may be volatilized. This difficulty may be avoided by first displacing the halides with nitric acid. Salts of acids containing arsenic or sulfur are reduced to arsenides or sulfides and then converted to borates by adding glucose along with the boric acid before fusing. (A nickel dish is used for arsenic compounds.) For each milliequivalent of salt to be transformed one takes 0.4–0.5 g. of boric acid and 1 g. of glucose. The charred mixture is ground to a fine powder, reheated, cooled, and extracted with hot water. Any insoluble residue should be returned to the dish and burned down again. Alkaline earths interfere; in their absence the method is accurate to within about 0.5%.

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[42] H. Schäfer and A. Sieverts, *Z. anal. Chem.*, **121**, 170 (1941); *Chem. Abstracts*, **35**, 5062 (1941).

[43] E. Schulek and I. Szlatinay, *Z. anal. Chem.*, **112**, 336 (1938).

Determination of Germanium: Tchakirian[44] observed that germanium dioxide forms with polyvalent alcohols a monobasic acid complex, which can be titrated with alkali to phenolphthalein. Poluektoff[45] applied the method to the determination of from 1–50 mg. of germanium (as sodium germanate) in 10 ml. of solution. The latter is weakly acidified with sulfuric acid, boiled 5 or 10 minutes to expel carbon dioxide, cooled under protection of a soda–lime tube, and neutralized with 0.1 N alkali to a yellow color with *p*-nitrophenol (probably methyl red would be equally satisfactory). After addition of 0.5–0.7 g. of mannitol the solution is titrated to the color change of phenolphthalein. More mannitol is then added and the titration continued further if necessary. For amounts of from 50 down to 5 mg. of germanium the results are accurate to within 0.5–1.0%. With smaller amounts the accuracy is lower.

Hydrofluoric and Hydrofluosilicic Acids: Hydrofluoric acid has an ionization constant of 3.7×10^{-4} and may therefore be titrated accurately with phenolphthalein as indicator. Since the acid attacks glass, noble metal vessels or glass flasks coated with paraffin or wax are required.

Siegel[46] determines fluoride in alkali fluoride solutions by adding freshly precipitated, neutral silica gel and titrating with hydrochloric acid to a permanent red color with methyl red:

$$6F^- + SiO_2 + 4H^+ \rightarrow SiF_6^{=} + 2H_2O$$

At the beginning the acid is consumed rapidly, but the reaction is slower toward the end. A necessary condition is that the solution contain only alkali or ammonium salts. In the presence of calcium, precipitation of calcium fluosilicate causes the acid color to appear much too soon. Since fluosilicate solutions react weakly acid to methyl orange (see below), one would expect that the end-point would not be sharp and that methyl orange would be more suitable than methyl red.

Commercial hydrofluoric acid ordinarily contains a little hydrofluosilicic acid and the determination of either acid in the presence of the other is difficult. Of the extensive literature on the subject, the earlier procedures give unsatisfactory results. Hydrofluosilicic acid is a strong electrolyte, yet solutions of its salts are not neutral because of a hydrolysis reaction:

$$SiF_6^{=} + 2H_2O \rightleftarrows SiO_2 + 4H^+ + 6F^-$$

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[44] A. Tchakirian, *Compt. rend.*, **187**, 229 (1928).

[45] N. S. Poluektoff, *Z. anal. Chem.*, **105**, 23 (1936).

[46] W. Siegel, *Z. angew. Chem.*, **42**, 856 (1929).

The fluoride and hydrogen ions also maintain an equilibrium:

$$H^+ + F^- \rightleftarrows HF$$

According to the author's observations, alkali fluosilicate solutions between 0.05 and 0.0025 M show a constant p_H of 3.5, while in 0.0001 M solution the p_H increases to 3.95.

It is possible to determine hydrofluosilicic acid as a dibasic acid by titrating to a p_T of 3.5 with methyl yellow as indicator, yet the end-point is not sharp and the accuracy is poor. Titration to phenolphthalein is much better; the acid then behaves as though hexabasic since fluosilicate ions react with alkali:

$$SiF_6^{=} + 4OH^- \rightarrow SiO_2 + 6F^- + 2H_2O$$

In the literature it is prescribed that the solution be boiled for five minutes with excess alkali and then titrated back. According to the author's experience the direct titration also yields good results if one titrates at boiling temperature to the first rose color. The change is not sharp, apparently because the precipitated silicic acid adsorbs some alkali. Alkaline earth salts interfere by reacting with silicic acid and liberating hydrogen ions. The boiling must be carried out in platinum or silver vessels.

Hydrofluoric and *hydrofluosilicic* acids may readily be determined together in this way. To determine one of the two in the mixture is more difficult. As an approximation the hydrofluosilicic acid may be titrated, according to Katz,[47] with a weak base (pyridine or aniline) and with methyl yellow as indicator. The procedure gives unsatisfactory results, however, and Katz sought to improve it by titrating in alcoholic solution in the presence of much potassium salt.

Under these conditions potassium fluosilicate has such a low solubility that it separates out and the reaction with alkali no longer occurs. To 5 ml. of the fluosilicic acid solution Katz adds 5 ml. of 2 N potassium chloride and enough alcohol to make its final concentration 40–50%, then he titrates to the rose color of phenolphthalein with 2 N alkali. A direct titration of the total acidity is also made as described above and the difference is calculated as hydrofluosilicic acid (equivalent weight = $\frac{1}{2}$ molecular weight). Because part of the hydrofluoric acid is bound by potassium fluosilicate as "acid of crystallization," a correction has to be applied to the result. The magnitude of this correction depends upon the quantity of each acid present. Katz determined and tabulated the corrections for various conditions.[48]

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[47] J. Katz, *Chem.-Ztg.*, **28**, 356, 387 (1904). See also S. Hönig-Szabadka, *ibid.*, **31**, 1207 (1907), R. H. Carter and R. C. Roark, *J. Econ. Entomol.*, **21**, 762 (1928).

Geffcken and Hamann[49] make use of the fact that the previously mentioned reaction between fluosilicate ions and alkali is reversible. For the titration of hydrofluoric acid they employ as reagent a 1 N potassium silicate solution, which contains silica in a very reactive form. In the presence of potassium chloride and alcohol, potassium fluosilicate is precipitated from both the hydrofluoric and hydrofluosilicic acids initially present:

$$\text{I.}\quad 6HF + K_2SiO_3 \rightarrow K_2SiF_6 + 3H_2O$$
$$H_2SiF_6 + K_2SiO_3 \rightarrow K_2SiF_6 + H_2SiO_3$$

Another equal portion is titrated in the same way with 1 N potassium hydroxide:

$$\text{II.}\quad 6HF + 6KOH \rightarrow 6KF + 3H_2O$$
$$H_2SiF_6 + 2KOH \rightarrow K_2SiF_6 + 2H_2O$$

In each of these titrations duplicate samples containing about 10 ml. of 1 N fluoride are treated with the same amounts of hydrochloric acid (about 5 ml. of 4 N, or enough to liberate the free acids), 20 ml. of alcohol and a few drops of bromocresol purple indicator, and the titration with either hydroxide or silicate is carried to a change from red to green. The number of equivalents of fluoride present is three halves of the difference between the numbers of equivalents of hydroxide and silicate taken. Titrations with silicate should be conducted slowly since the formation of fluosilicate requires a certain time.

For the determination of fluosilicate the suspension remaining from titration II is diluted with 100 ml. of water, heated to boiling and titrated hot with potassium hydroxide to an end-point with α-naphtholphthalein, thus hydrolyzing the fluosilicate ions (*cf.* p. 121).

The author has obtained satisfactory results by the following method which depends upon the volatility of hydrogen fluoride:

A portion of the mixture of the two acids is titrated at boiling in a platinum vessel, to the phenolphthalein end-point.

$$HF + OH^- \rightleftarrows F^- + H_2O$$
$$H_2SiF_6 + 6OH^- \rightleftarrows 6F^- + SiO_2 + 4H_2O$$

To another portion, also in platinum, a little hydrochloric acid and about one gram of sodium chloride are added and the mixture is evaporated to dryness on a water bath. The residue is moistened with several milliliters of water and again evaporated. By this procedure hydrofluoric acid is completely volatilized leaving the sodium fluosilicate together with sodium chloride. The fluosilicate is then titrated to a phenolphthalein end-point at boiling, as has already been described:

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[48] The method has been criticized by L. J. Hudleston and H. Bassett, *J. Chem. Soc.*, **119**, 403 (1921). See also A. Greeff, *Ber.*, **46**, 2511 (1913); J. G. Dinwiddie, *Am. J. Sci.*, **42**, 421 (1916); P. H. M. Brinton, L. A. Sarver, and A. E. Stoppel, *Ind. Eng. Chem.*, **15**, 1080 (1923); E. D. Garcia, *Chem. Abstracts*, **15**, 3801 (1921).

[49] W. Geffcken and H. Hamann, *Z. anal. Chem.*, **114**, 15 (1938).

$$SiF_6^{=} + 4OH^- \rightleftarrows 6\ F^- + SiO_2 + 2H_2O$$

Determination of Alkali Metals as Fluosilicates: It has been shown by Treadwell and König[50] that the chlorides and nitrates of sodium, potassium, and lithium can easily be converted into fluosilicates by evaporating to dryness in a platinum dish with a threefold excess of silica gel and a larger excess of hydrofluoric acid (1 to 2 ml. of 40% acid per 0.1 g. of silicon dioxide). Both of the reagents must be pure; methods of preparation are described in the original article. After the residue has been heated for an hour or two at 120°C. and taken up in 10 ml. of warm water, it may be titrated by the method of Schucht and Möller,[51] in which 10–25 ml. of neutral 4 N calcium chloride is added and the mixture is boiled, then neutralized with standard alkali to a p_H of 5.3 (bromocresol purple or chlorophenol red as indicator):

$$SiF_6^{=} + 3Ca^{++} + 3H_2O \rightarrow 3CaF_2 + H_2SiO_3 + 4H^+$$
$$4H^+ + 4OH^- \rightarrow 4H_2O$$

The procedure is capable of giving accurate results and may be used for the indirect analysis of alkali mixtures. The metals must be present as chlorides or nitrates, and magnesium must be removed beforehand, for example with oxine. Ammonium salts and organic substances are destroyed by heating. For micro determinations the fluoride of the fluosilicate residue may be titrated with thorium nitrate or zirconium chloride solution (pp. 321, 325).

Determination of Silica in Silicates: The fluosilicate titration has been applied by Tananaeff and Babko[52] to the determination of silica. The sample after potassium carbonate fusion is taken up with an excess of hydrochloric acid and ammonium fluoride, silica being precipitated as potassium fluosilicate. After addition of calcium chloride to the precipitate, the mixture is titrated with 0.5 N sodium hydroxide to the color change of methyl red. Further testing of the method, perhaps with substitution of the direct phenolphthalein titration, would be desirable.

Organic Hydroxy Acids: From the ionization constants (Vol. I, tables, p. 283) it is evident that organic hydroxy acids may be classed as weak or moderately strong (K_2 also being considered in the cases of dibasic acids). For neutralization of all the acid groups phenolphthalein or a similar indicator (thymol blue) should be employed; with an alkali-sensitive indicator like methyl orange one obtains incorrect results because the change occurs much too soon and is not at all sharp.

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[50] W. D. Treadwell and W. König, *Helv. Chim. Acta*, **16**, 1201 (1933).

[51] L. Schucht and W. Möller, *Ber.*, **39**, 3693 (1906).

[52] N. A. Tananaeff and A. K. Babko, *Z. anal. Chem.*, **82**, 145 (1930).

Studies by Bruhns[53] have shown that salts of alkaline earths or heavy metals increase the acid character of hydroxy acids considerably. These cations form complexes with the anions of the acids and this fact may be used to advantage in titrating such acids with methyl orange or methyl yellow as indicator (see also oxalic acid, p. 98). According to the author's determinations addition of calcium chloride is most satisfactory, in amounts of 4–5 g. of the crystallized salt per 25 ml. of 0.1 N acid solution. The end-point is not sharp nor the accuracy great. If one titrates to the water color of the indicator, tartaric, citric, malic, and lactic acids may be determined to within about 0.5%. A comparison solution of the indicator in water should be used. Salicylic acid may be titrated sharply in the presence of much calcium salt. In this case methyl red gives a better end-point than methyl yellow.

Higher Fatty Acids: Upon neutralization of the higher fatty acids there are formed soaps, which are strongly hydrolyzed in aqueous solution. This hydrolysis is less dependent upon the weakness of the acid, as is usually assumed, than upon its slight solubility. Dissolved in a suitable solvent like alcohol the higher fatty acids have about the same ionization constants as lower members of the series. Therefore they can be neutralized to phenolphthalein or thymol blue with sufficient sharpness.

Procedure: A weighed amount of the fatty acid is dissolved in enough alcohol—neutral to phenolphthalein—to make the concentration of the latter at least 50% at the end-point. The alcoholic solution is then titrated with aqueous alkali against phenolphthalein as indicator.

Notes: (1) For the titration of fatty acids in fats and oils, reference is made to the treatise of Grün.[54] If the fat is dark in color, thymol blue may be used to advantage in place of phenolphthalein, its change to blue being more distinct.

(2) Alcohol lowers the ionization constants both of the weak acids and of the indicators. In addition, the ion product of water becomes smaller with increasing alcohol concentration.[55] For the calculation of titration errors

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[53] G. Bruhns, *Z. anal. Chem.*, **55**, 321 (1916).

[54] A. Grün, *Analyse der Fette und Wachse.* Vol. 1, Springer, Berlin 1925, p. 140.

[55] I. M. Kolthoff, *Acid-Base Indicators*, translated by C. Rosenblum. Macmillan, New York 1937, pp. 96, 214.

in alcoholic solution, therefore, one would have to use constants differing from those applicable in aqueous solutions. The neutralization curves of fatty acids in alcohol as determined potentiometrically by Bishop, Kittredge, and Hildebrand[56] are of interest in this connection.

(3) Titrations of weak acids and bases in water–alcohol mixtures have been investigated thoroughly by Baggesgaard-Rasmussen.[57] He concluded that phenolphthalein is a suitable indicator for titrating weak acids. The main advantage of having alcohol in the mixture is that it is a better solvent than water. In the determination of bases, addition of alcohol is generally detrimental, but in the titration of salts of weak bases (alkaloid hydrochlorides, etc.) ethanol offers advantages, especially when used in high concentration.

3. Titration of Weak Bases with Strong Acids.

—What was said at the beginning of the preceding section concerning the titration of weak acids with strong bases holds as well, *mutatis mutandis*, for the determination of weak bases with strong acids. Here also a table has been prepared, showing under what conditions a base of known ionization constant may be titrated satisfactorily.

HYDROGEN-ION CONCENTRATIONS NEAR THE EQUIVALENCE-POINT IN TITRATIONS OF WEAK BASES WITH STRONG ACIDS

Ionization Constant, K_b	Titration of 1 N Solutions			Titration of 0.1 N Solutions			Titration of 0.01 N Solutions		
	p_H 0.2% before p_T	p_T	p_H 0.2% after p_T	p_H 0.2% before p_T	p_T	p_H 0.2% after p_T	p_H 0.2% before p_T	p_T	p_H 0.2% after p_T
10^{-3}	8.5	5.7	3.0	8.4	6.2	4.0	8.3	6.65	5.0
10^{-4}	7.5	5.2	3.0	7.4	5.7	4.0	7.3	6.15	5.0
10^{-5}	6.5	4.7	3.0	6.4	5.2	4.0	6.3	5.65	5.0
10^{-6}	5.5	4.2	3.0	5.4	4.7	4.0	5.43	5.15	4.86
10^{-7}	4.5	3.7	3.0	4.44	4.2	3.87	4.75	4.65	4.54
10^{-8}	3.56	3.2	2.9	3.79	3.7	3.58	4.17	4.15	4.13
10^{-9}	2.84	2.7	2.55	3.22	3.2	3.18	3.65	3.65	3.65
10^{-10}	2.26	2.2	2.15						

Under p_T are listed the equivalence-point hydrogen exponents calculated for titrations of various weak bases with strong acids. The data again apply at 24°C. ($K_w = 10^{-14}$), and the activity coefficients assumed for the salts are the same as those on page 112. From the p_H values shown for states 0.2% before and 0.2% after the equivalence-point in each case, one can tell whether or not a given alkaline solution can be titrated with sufficient accuracy, using an indicator of known transition interval.

Titration of 0.01 N Bases with 0.01 N Hydrochloric Acid: By titrating to the water color with methyl red as indicator, the error of a determination can be kept below 0.2% provided that the value of K_b is greater than 3 × 10^{-6}. With weaker bases an appropriate reference solution should be employed; under these conditions one can titrate a base of ionization constant 10^{-7} easily to within 0.5% For use between p_T values of 4.8 and 4.2, methyl red and bromocresol green are best suited as indicators.

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[56] E. R. Bishop, E. B. Kittredge, and J. H. Hildebrand, *J. Am. Chem. Soc.*, 44, 136 (1922).

[57] H. Baggesgaard-Rasmussen, *Z. anal. Chem.*, 105, 269 (1936).

Titration of 0.1 N Bases with 0.1 N Hydrochloric Acid: Bases with ionization constants greater than 10^{-6} may be titrated to within 0.2% using methyl yellow, methyl orange, or bromophenol blue, without a comparison solution. With a suitable solution for reference, bases having constants down to 10^{-8} may be titrated with not more than about 0.5% error. Those whose constants are still smaller cannot be titrated accurately in 0.1 N solution.

Titration of 1 N Bases with 1 N Hydrochloric Acid: Using methyl yellow as indicator it is possible to titrate, without a reference solution, bases whose constants are greater than 10^{-7}. If the constants are smaller, tropeolin 00 or thymol blue should be used with a standard for color comparison. Thus bases of constants down to 5×10^{-10} can still be titrated with an error of not more than 0.5%.

Practical application of these calculations has been made[58] in the titration of aniline ($K_b = 4.6 \times 10^{-10}$) and of urotropine (hexamethylenetetramine, $K_b = 8.4 \times 10^{-10}$). In the titration of 1 N aniline (2.325 g. + 25 ml. of water) a reference solution composed of 50 ml. of 0.0028 N hydrochloric acid was chosen. The titration values were reproducible to within 0.2%. From the above it is apparent that end-points obtained with methyl orange or congo red occur too soon, yet in the literature these indicators have been specified for the purpose. In titrations of 1 N urotropine a 0.0022 N solution of hydrochloric acid may be used for reference and the accuracy is the same.

In order to titrate solutions of volatile bases like ammonia and the lower amines, additional precautions are necessary to prevent losses. After a rough preliminary titration a sample is pipetted into an excess of acid which is then titrated back.[59] Pipetting by means of pressure rather than suction is desirable with strong solutions.

Titration of Alkaloids:[60] In the following table are assembled p_T values for the titration of 0.1 N and 0.01 N alkaloids. The data are based mainly on ionization constants as given in Volume I, p. 285, and on a value of 14.0 for p_w. Some of the alkaloids are diacid bases; for these there is also given the p_{T} at the first equivalence-point, corresponding to formation of a basic salt. Such compounds really belong in section 5, p. 130, but are kept with the other alkaloids for convenience.

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[58] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **115**, 177 (1921).

[59] *Cf.* H. Menzel, *Z. anorg. allgem. Chem.*, **164**, 4 (1927).

[60] On this subject, which is of great practical importance in pharmaceutical chemistry, there is given in the literature much information that is incorrect or only partially correct. General rules cannot readily be applied to the alkaloids and they have to be treated more or less individually. The completeness of the discussion here is limited by lack of space; for further details and literature references see I. M. Kolthoff, *Biochem. Z.*, **162**, 289 (1925); F. Müller, *Z. Elektrochem.*, **30**, 587 (1924).

TITRATION EXPONENTS FOR ALKALOIDS IN WATER AT 24°C.

Alkaloid	p_{T} of the normal salt in titration of solutions		p_{T} of the basic salt	Alkaloid	p_{T} of the normal salt in titration of solutions		p_{T} of the basic salt
	0.1 N	*0.01 N*			*0.1 N*	*0.01 N*	
Aconitine	4.7	5.2		Narcotine	3.75	4.25	
Apomorphine	4.15	4.65		Nicotine	2.15	2.65	5.6
Arecoline	4.2	4.7		Novocaine base	2.35	2.85	5.8
Atropine	5.4	5.9		Papaverine	3.6	4.1	
Berberine	6.9	6.95		Pelletierine	5.25	5.75	
Brucine	(1.75)	(2.3)	5.35	Physostigmine			4.8
Cinchonidine	2.65	3.15	6.3	Pilocarpine	(1.35)	(1.85)	4.35
Cinchonine	2.7	3.2	6.3	Piperazine	3.45	3.95	7.7
Cocaine	4.85	5.35		Piperidine	(Strong base)		
Codeine	4.65	5.15		Pyridine	3.2	3.7	
Coniine	(Strong base)			Quinidine	2.65	3.15	6.5
Cytisine			4.6	Quinine	2.8	3.3	6.3
Dionine	4.6	5.1		Quinoline	2.9	3.40	
Emetine	4.35	4.85	8.0	Solanine	4.35	4.85	
Euquinine	2.3	2.8	5.0	Sparteine	2.95	3.45	
Hydrastine	3.75	4.25		Strychnine	(1.7)	(2.3)	5.35
Morphine	4.55	5.05		Thebaine	4.6	5.1	
Narceine	2.3	2.8		Veratrine	5.05	5.55	

Consideration of the monoacid alkaloids shows that aconitine, atropine, berberine, cocaine, codeine, coniine, dionine, morphine, pelletierine, piperidine, thebaine, and veratrine in 0.01 N solutions may be titrated accurately to methyl red. The same is also true of 0.1 N solutions, for which methyl yellow may also be used. In order to titrate 0.01 N arecoline or solanine a comparison solution is necessary; no accurate titration of hydrastine, narcotine, or papaverine is possible at this dilution. In the latter cases, however, titrations of 0.1 N solutions can be carried out successfully with the aid of reference solutions and with methyl yellow as indicator.

The diacid alkaloids are generally determined only as monoacid bases, their second ionization constants being too small to permit accurate neutralization. One exception is emetine, which can be titrated as either a monoacid or a diacid base. The first end-point with cresol red indicator (at a p_{T} of 8.0) is not sharp, but the second, with methyl red, yields a quite accurate result. Determinations of the cinchona alkaloids and of brucine, strychnine, nicotine, and novocaine base are best carried out using methyl red. In the case of the cinchona compounds the end-point is not very sharp but can be recognized easily within 1% if taken at the first change from the yellow color. In the literature it is frequently stated that quinine, etc., can be determined as diacid bases using methyl orange. The end-point comes too soon, giving inaccurate results even with a standard for comparison. Determinations as the monoacid compounds are preferable. Methyl yellow serves as indicator for titrations of cytisine, physostigmine, and pilocarpine. Sparteine may be titrated accurately to a p_T of 8.4 with phenolphthalein. Phenol red or cresol red is more suitable for piperazine, with a p_T of 7.7.

Quinine dissolved in glacial acetic acid can be titrated as a diacid base with a solution of perchloric acid in the same solvent, using α-naphtholbenzein as indicator.[61] The end-point is reached when the indicator has a blue-green color.

A practical difficulty in titrating alkaloids is that most of the free bases are only slightly soluble in water. If one is assaying a drug[62] the free alkaloid is usually extracted from alkaline medium with a suitable solvent, which is then evaporated. Since the residue does not dissolve readily in water, direct titration is difficult. However, a known amount of acid may be added and the excess titrated back with alkali, all of the above considerations then applying. Even this procedure fails in some cases. Thus Schoorl[63] found that an acidified solution of euquinine has to be diluted to 0.001 M before back-titration to methyl red, in order to prevent precipitation of the free base, whereas aristochine precipitates even at this dilution.

An alternative suggestion is to dissolve the alkaloid in alcohol and titrate directly with acid. As has previously been noted (p. 124), alcohol lowers the ionization constants both of the weak base and of the indicator, as well as the ion product of water. Most alkaloids which can be titrated sharply in water (using methyl red) can no longer be determined accurately in 50% alcohol; this is true especially of 0.01 N solutions. The following illustration may be given in explanation:

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[61] R. L. Herd, *J. Am. Pharm. Assoc.*, **31**, 9 (1942).

[62] C. Kippenberger, *Z. anal. Chem.*, **39**, 201 (1900). J. Messner, *Z. angew. Chem.*, **16**, 444 (1903). E. Rupp and K. Seegers, *Apoth. Ztg.*, **22**, 748 (1907). H. Baggesgaard-Rasmussen and S. A. Schou, *Z. Elektrochem.*, **31**, 189 (1925). A. R. von Korczynski, *Die Methoden der exakten quantitativen Bestimmung der Alkaloide*, Bornträger, Berlin 1913, p. 1. H. Bauer, *Analytische Chemie der Alkaloide*, Bornträger, Berlin 1921, p. 46.

[63] N. Schoorl, *Pharm. Weekblad*, **76**, 1513 (1939).

A 0.05 M solution of cocaine hydrochloride shows a p_H of 4.7 with methyl red. The addition of 5 ml. of water and 0.05 ml. of 0.01 N sodium hydroxide to 5 ml. of the solution changes the color completely to yellow. A mixture of 5 ml. of the original solution with 5 ml. of 96% alcohol requires 1 ml. of 0.01 N alkali before the color changes entirely from orange to yellow. Therefore if an alcoholic solution of cocaine is titrated with acid to a methyl red end-point, the latter appears too early and is not sharp. The use of bromophenol blue is better in this case, with titration from the blue color to green or yellow. Many other alkaloids behave similarly. In 50% alcoholic solutions aconitine, apomorphine, atropine, brucine, codeine, emetine, morphine, strychnine, tropacocaine, and veratrine can be titrated accurately to bromophenol blue.

Quinine and the other cinchona alkaloids may be titrated to a p_T of 6.2 using methyl red, or more sharply with bromocresol purple to the change from purple-blue to yellow. If the alkaloid in question is volatile, the solvent used for extraction should not be removed by evaporation. In its presence methyl orange may be employed as indicator.

Determination of Nickel with Dicyandiamidine: An application of the acidimetric titration of a weak base was made by Fluch[64] in a method for determining nickel as its dicyandiamidine salt, $Ni(C_2H_5N_4O)_2 \cdot 2H_2O$. The reagent behaves as a monoacid base toward methyl red and according to Fluch may be titrated sharply using this indicator. The nickel compound, precipitated with dicyandiamidine and alkali, is washed with alcohol and dissolved in an excess of acid, which is titrated back with sodium hydroxide to the first change from the red color of methyl red:

$$Ni(C_2H_5N_4O)_2 + 4HCl \rightarrow NiCl_2 + 2C_2H_6N_4O \cdot HCl$$

Each milliliter of 0.1 N hydrochloric acid corresponds to 1.467 mg. nickel. Dubský and Hauer[65] have adapted the procedure to the micro determination of nickel.

4. Titration of Weak Acids with Weak Bases.—In general weak bases are titrated with strong acids, and weak acids with strong bases, since under these conditions the greatest change in p_H at the equivalence-point can be obtained. Yet in effect the problem of titrating a weak acid with a weak base is encountered when a weak acid has to be determined in the presence of the cations of a weak base, for example, acetic acid in the presence of ammonium chloride, or conversely, ammonium hydroxide in the presence of sodium acetate. The task of determining free acidity or alkalinity in ammonium acetate or in the ammonium salt of another weak acid is also of practical importance. In order to learn what indicator should be used and how accurately the titration may be made, one must know the p_H at the equivalence-point itself and the course of the p_H before and after. These questions have been discussed in Volume I, pp. 23–24 and 55, where it was seen that the solution of a salt of a weak acid and weak base has a p_H almost independent of the dilution:

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[64] P. Fluch, *Z. anal. Chem.*, **69**, 232 (1926).

[65] J. V. Dubský and E. Hauer, *Mikrochemie*, **12**, 321 (1933).

$$p_H = 7 + \tfrac{1}{2}p_a - \tfrac{1}{2}p_b \text{ (at 24°C).}$$

The following table lists p_H values and suitable indicators for direct or reverse titrations of weak acids with ammonia. Since the changes in p_H near the equivalence-point are small, it is always necessary to use a reference solution. Under these conditions it is possible to titrate to within about 0.5%. Mixed indicators can be used to advantage in these titrations.

TITRATION OF WEAK ACIDS WITH AMMONIA, OR VICE VERSA

Acid	p_T	Indicator
Acetic	7.0	Phenol red, neutral red
Benzoic	6.7	Bromothymol blue, chlorophenol red
Citric	7.4	Phenol red, neutral red
Formic	6.5	Bromothymol blue, chlorophenol red
Lactic	6.5	Bromothymol blue, chlorophenol red
Oxalic	6.9	Bromothymol blue, phenol red
Phthalic	7.2	Phenol red, neutral red
Salicylic	6.3	Bromothymol blue, chlorophenol red
Succinic	6.7	Bromothymol blue, chlorophenol red
Tartaric	6.65	Bromothymol blue.

5. Polybasic Acids and Polyacid Bases.—In order to titrate all of the acid groups of a polybasic acid, the titration exponent which should be attained is determined by the value of the last ionization constant (for example, by K_3 in the case of citric acid); all the considerations of Section 2 apply. The situation is different if the titration is to be carried only to the formation of an acid salt. Then the p_H at the first equivalence-point is determined by the first and second ionization constants:[66]

$$p_H = \tfrac{1}{2}(\ p_{K_1} + p_{K_2})$$

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[66] See Volume I, pp. 26–31, 56–58, 151–153, for the derivation of theoretical principles employed in this section.

This value of the p_H corresponds to the titration exponent. If the ratio of K_1 to K_2 is smaller than 1000, no satisfactory results can be obtained as the p_H changes too gradually in the vicinity of the equivalence-point. For this reason the ordinary dibasic organic acids cannot in general be titrated accurately to their acid salts. Some special cases of interest in inorganic analysis will be discussed in the following paragraphs.

Carbonic Acid: $K_1 = 3.0 \times 10^{-7}$, $K_2 = 6 \times 10^{-11}$. From the table on p. 113 one can see that carbonic acid cannot be titrated directly as a dibasic acid; its second ionization constant is too small and accordingly the normal carbonate is too strongly hydrolyzed. However, determination as a dibasic acid is possible if the carbonate ion is removed from solution by precipitation with an alkaline earth salt, generally with a salt of barium. Alternatively an excess of barium hydroxide solution (also containing barium chloride) may be added and titrated back without previous filtration, using phenolphthalein.

Procedure for Determination of Bicarbonate in Sodium Bicarbonate or Carbonate: Prepare the sample as an approximately 0.1 N bicarbonate solution in a stoppered volumetric flask, without allowing the temperature to rise. To 25 ml. of this solution add 30 ml. of 0.1 N alkali (carbonate-free) and 10 ml. of 10% barium chloride. Titrate back to phenolphthalein with 0.1 N acid and also titrate a blank containing the same amount of alkali and barium chloride. The difference represents bicarbonate, each ml. of 0.1 N solution corresponding to 8.4 mg. of the sodium salt.

Direct Titration of Carbonic Acid as a Monobasic Acid: To estimate the accuracy of this practically important titration, it is necessary to know p_T and the changes in p_H near the equivalence-point.

$$p_T = \tfrac{1}{2}(p_{K_1} + p_{K_2}) = 8.35$$

For calculating changes in hydrogen-ion concentrations near the equivalence-point one cannot apply directly the simple equations:

$$[H^+] = \frac{[H_2CO_3]K_1}{[HCO_3^-]} \qquad \text{(acid side)}$$

and

$$[H^+] = \frac{[HCO_3^-]K_2}{[CO_3^=]} \qquad \text{(alkaline side)}$$

because of hydrolysis effects. For both cases there apply more complicated expressions which take hydrolysis into account; as an approximation the quadratic equation 53, Volume I, p. 30, may be employed.[67] However, experimental determination of the p_H on either side of the equivalence-point is more to be recommended. By colorimetric methods the p_H values have been found for 0.1 N and 0.01 N sodium bicarbonate solutions, alone and after slight additions of hydrochloric acid or sodium hydroxide. They are as follows:

Per Cent of Excess Acid	p_H	Per Cent of Excess Base	p_H
0	8.35	0	8.35
1	8.15	1	8.7
3	7.9	5	9.0
5	7.8	10	9.2

These data show that the change at the first equivalence-point cannot be sharp with any indicator. For example, if one attempts to titrate carbonate to bicarbonate with acid using phenolphthalein as indicator, the red color begins to fade when only about 80% of the carbonate has been converted into bicarbonate; furthermore the solution does not become entirely colorless until a 3–5% excess of acid has been added. The use of a reference solution makes possible better results, correct to within about 0.5%.

Procedure for the Titration of Carbonate to Bicarbonate: To a convenient amount of carbonate solution add 1 or 2 drops of 1% phenolphthalein and titrate slowly with shaking until the color lightens to a rose tint. Prepare in a similar vessel an equal volume of pure sodium bicarbonate solution with the same quantity of indicator and continue titrating until the colors match. Thymol blue is satisfactory in place of phenolphthalein; one titrates to a green and compares with the corresponding bicarbonate solution. At the end-point the color is yellow with a tinge of green.

Notes: (1) In case the titration is carried to complete decoloration of phenolphthalein or to the yellow of thymol blue, without a reference solution, the titration error amounts to 3–5%. Küster[68] repressed the hydrolysis of bicarbonate by adding an excess of alkali chloride and working at 0°C. According to Lunge and Lohöfer[69] one may add 3.5 moles of alkali chloride for each mole of carbonate and titrate at room temperature. This has not been confirmed by the authors.

Better results are obtained in the presence of glycerin.[70] To 25 ml. of carbonate are added 10 ml. of neutral glycerin and the solution is titrated until colorless to phenolphthalein. The result is not accurate to better than 1 or 2% unless a comparison solution is used.

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[67] See also F. Auerbach, *Z. angew. Chem.*, **25**, 1722 (1912); F. Auerbach and H. Pick, *Arb. kaiserl. Gesundh.*, **38**, 243 (1911); H. N. McCoy, *Am. Chem. J.*, **31**, 512 (1904); I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **100**, 143 (1917); *Z. Untersuch. Nahr. u. Genussm.*, **41**, 121 (1921).

[68] F. W. Küster, *Z. anorg. Chem.*, **13**, 142 (1897).

[69] G. Lunge and W. Lohöfer, *Z. angew. Chem.*, **14**, 1130 (1901).

[70] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **100**, 156 (1917).

(2) In order to make possible a sharper perception of the end-point without use of a reference standard, Simpson[71] utilized a mixed indicator (see also p. 56) composed of 6 volumes of 0.1% thymol blue and 1 volume of 0.1% cresol red. This has a dark purple color in the carbonate solution, changing to blue near the equivalence-point. The end-point is reached when the solution assumes a rose color; this goes over to orange-yellow with further addition of acid. *The method may be recommended highly, as results accurate to within 0.5% can be obtained after some practice.* For example, in the titration of 25 ml. of 0.05 M soda containing 5 drops of the indicator, the blue color began to fade after addition of 12.4 ml. of 0.1 N hydrochloric acid and the rose color appeared between 12.5 and 12.6 ml., changing towards orange-yellow with 12.7 ml. If only a little carbonate is present with much bicarbonate, however, the titration is inexact.

(3) If in titrating carbonate the acid is added very rapidly, too much is required. Local excesses of the acid react with bicarbonate to form carbonic acid which is transformed only slowly into bicarbonate by the remaining carbonate (see below). In order to prevent loss of carbon dioxide, Čûta and Kámen[72] recommend performing the titration in a Nessler tube and covering the solution with a layer of benzene.

Titration of Free Carbonic Acid to Bicarbonate: The reaction between carbon dioxide and hydroxyl ions does not proceed instantaneously, but rather slowly. Upon this fact depends the long-known fading of the red phenolphthalein color during titrations of carbon dioxide solutions. For an explanation of the fading we are indebted to Vorländer and Struba[73] and especially to Thiele and his associates.[74]

Carbonic acid in water exists only to a small extent as H_2CO_3, being mostly in the form of its anhydride CO_2 which becomes hydrated very slowly:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

Since the carbon dioxide is not itself an acid, it must first be converted to H_2CO_3, after which it can react practically instantaneously with sodium hydroxide. Thiele and Strohecker[74] showed that at 4°C. only 0.67% of the total amount of carbon dioxide is present as H_2CO_3 and that in the concentration used by them the latter is 91% ionized.

An ionization constant of carbonic acid as ordinarily determined is only an *apparent* one, for in its calculation the value taken for $[H_2CO_3]$ is actually the total quantity $[CO_2 + H_2CO_3]$. Upon substituting the much smaller real value, the *true* ionization constant is found to be larger; Thiele and Strohecker obtained a figure of 5×10^{-4}. Carbonic acid therefore is a fairly strong acid ("hydroxy formic acid").

For the reaction

$$H_2CO_3 \rightleftarrows CO_2 + H_2O$$

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[71] S. G. Simpson, *Ind. Eng. Chem.*, **16**, 709 (1924).

[72] F. Čûta and K. Kámen, *Collection Czechoslov. Chem. Commun.*, **11**, 77 (1939).

[73] D. Vorländer and W. Struba, *Ber.*, **46**, 172 (1913).

[74] A. Thiele, *Ber.*, **46**, 241, 867 (1913). A. Thiele and R. Strohecker, *Ber.*, **47**, 945, 1061 (1914). See also J. W. McBain, *J. Chem. Soc.*, **101**, 814 (1912); L. Pusch, *Dissertation*, Berlin 1916; *Z. Elektrochem.*, **22**, 206 (1916); C. Faurholt, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **3**, No. 20 (1921); *J. chim. phys.*, **21**, 400 (1924); **22**, 1 (1925); A. Eucken and H. G. Grützner, *Z. phys. Chem.*, **125**, 363 (1927).

Saal[75] found at 13.7°C. the equilibrium constant

$$K' = \frac{[H_2CO_3]}{[CO_2][H_2O]} = 1.1 \times 10^{-3}$$

From this the true ionization constant of H_2CO_3 is calculated to be 3.1×10^{-4} at 13.7°.

If one wishes to titrate free carbonic acid using phenolphthalein without a comparison solution, the amount of indicator taken is of importance,[76] because at a given hydrogen-ion concentration the intensity of color in the solution will depend upon the indicator concentration (*cf.* Vol. I, p. 95).

Procedure: To 100 ml. of solution add 1 ml. of 1% phenolphthalein and titrate with alkali until the rose color persists for five minutes. Since carbonic dioxide is so volatile, Winkler[76] recommends making the determination in slender glass-stoppered bottles of about 125 ml. capacity, with the 100 ml. level marked by a ring.

Notes: (1) The color of the indicator keeps fading until the permanent end-point is reached and therefore the bottle must be opened frequently for addition of more reagent. During this operation carbon dioxide may be lost; therefore a second determination should always be made, the amount of alkali used in the first analysis being added all at once and the titration then being completed carefully as above.

(2) As has already been mentioned, the first perceptible pink coloration of phenolphthalein develops a little before the equivalence-point. Too little alkali is therefore required and a corresponding correction should be applied. The magnitude of the correction depends upon the quantity of bicarbonate as well as upon the presence of alkaline earths. In the titration of drinking water, which generally contains calcium, magnesium, and an excess of bicarbonate, this correction may be appreciable. It increases with rising bicarbonate content and decreases with increasing hardness. Corrections determined experimentally by Kolthoff[76] are listed in the accompanying table.

CORRECTIONS (IN MILLILITERS OF 0.1 N ALKALI) FOR THE TITRATION OF CARBONIC ACID

a	Hardness in German Degrees[77]		
	0°	*10°*	*20°*
2	+0.04	0.0	−0.04
4	0.09	+0.05	0.0
6	0.13	0.1	+0.06
8	0.17	0.14	0.10

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[75] N. R. J. Saal, *Rec. trav. chim.*, 47, 264 (1928). See also A. R. Olson and P. V. Youle, *J. Am. Chem. Soc.*, 62, 1027 (1940).

[76] H. Noll, *Z. angew. Chem.*, 25, 998 (1912). J. Tillmans and O. Heublein, *Z. Untersuch. Nahr. u. Genussm.*, 24, 429 (1912). L. W. Winkler, *Z. anal. Chem.*, 53, 746 (1914). I. M. Kolthoff, *Z. Untersuch. Nahr. u. Genussm.*, 41, 97 (1921).

[77] One German degree of hardness is equivalent to 10 mg. CaO per liter.

Here a represents the number of milliliters of 0.1 N bicarbonate present per 100 ml. of solution at the first equivalence-point. This number is equal to the sum of two titrations on separate portions of sample, one with 0.1 N hydrochloric acid to methyl yellow and the other with 0.1 N alkali to phenolphthalein, which together give the quantity of bicarbonate at the equivalence-point.

(3) In place of sodium hydroxide one may titrate with sodium carbonate. This solution is especially to be recommended for the determination of very small amounts of carbonic acid, as in aerated distilled water. A sample of 1 or 2 liters is placed in a bottle of such size that it will be nearly filled. For each liter of water there is added 1 ml. of neutralized phenol red solution, prepared by dissolving 100 mg. of phenol red in 4.5 ml. of 0.1 N alkali and diluting to 100 ml. with water. Titration is made with 0.005 M sodium carbonate until the color remains red-violet.[78]

(4) A simple method for the determination of carbon dioxide in air has been described by Winkler.[79] To the air sample in a flask is added 10–20 ml. of alcohol previously neutralized to phenolphthalein, and the solution is titrated with 0.02 N sodium carbonate until a pale rose color remains after shaking. The titration requires only about 5 minutes, but precautions must be taken against entrance of carbon dioxide from the outside air.

Phosphoric Acid: $K_1 = 1.1 \times 10^{-2}$, $p_{K_1} = 1.96$
$K_2 = 1.95 \times 10^{-7}$, $p_{K_2} = 6.7$
$K_3 = 3.6 \times 10^{-13}$, $p_{K_3} = 12.44$

Titration as a Monobasic Acid: The titration exponent p_T calculated from the expression $\frac{1}{2}(p_{K_1} + p_{K_2})$ is equal to 4.35. Experimentally a value of 4.4–4.45 has been found by colorimetric tests on a solution of pure primary potassium phosphate with bromocresol green as indicator. At this p_H methyl orange would be almost completely converted into its alkaline form and might be expected to serve as a good indicator for the titration. Since the color is not quite a pure yellow at 4.4, it is best to employ a reference solution. The p_H change near the equivalence-point is large enough so that the error need not exceed 0.5%:

Solution	p_H	
25 ml. 0.1 M KH_2PO_4 + 1% excess acid	4.0	determined colorimetrically
25 ml. 0.1 M KH_2PO_4	4.45	
25 ml. 0.1 M KH_2PO_4 + 1% excess base	4.7	

Procedure: To the phosphoric acid solution add several drops of bromocresol green or methyl orange and titrate until the color matches that of a reference solution containing the same concentration of sodium dihydrogen phosphate and indicator.

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[78] I. M. Kolthoff, *Biochem. Z.*, **176**, 101 (1926).

[79] L. W. Winkler, *Z. anal. Chem.*, **92**, 23, 245 (1933); **100**, 29 (1935). See also Y. Kauko, *J. Sci. Agr. Soc. Finland*, **6**, 33 (1934); *Angew. Chem.*, **47**, 164 (1934).

Phosphoric Acid as a Dibasic Acid: This titration is less exact. A solution 0.05 M in disodium phosphate has a p_H of about 9.6 and therefore colors phenolphthalein a deep red. With this indicator the color change occurs about 7 % too soon. By adding enough sodium chloride to half saturate the solution, the hydrolysis may be strongly repressed[80] and the error cut to the order of 1%. Alternatively, thymolphthalein may be employed as indicator without the addition of salt.

Procedure 1: To the phosphoric acid or primary phosphate solution add phenolphthalein and enough sodium chloride to make the solution half saturated at the equivalence-point. Titrate with alkali to a pale rose color.

Procedure 2: Add several drops of thymolphthalein to the solution and titrate with sodium hydroxide to a weak blue color. With carbonate-free alkali it is possible to obtain results accurate to within 0.5–1%. (The color change is to a green if methyl orange is also present.)

Notes: (1) Sodium chloride should not be present during titration of phosphoric acid as a monobasic acid. The change would then come too late because the hydrogen-ion concentration of a primary phosphate solution is increased by alkali chlorides.

(2) Calamari and Hubata[81] modify Kolthoff's method by working with a completely saturated sodium chloride solution and titrating until the color matches that of a specially prepared reference solution. Allowing for salt effects on the indicators, a reference solution of p_H 3.62 is used for the first equivalence-point and one of 7.98 for the second, with bromophenol blue and cresol red, respectively, as indicators. The original paper should be consulted for details.

Phosphoric Acid as a Tribasic Acid: The third ionization constant is so small that the third acid group cannot be titrated directly. However, if trivalent phosphate ion is precipitated in the form of an insoluble salt, the determination can be carried out with phenolphthalein as indicator. Calcium chloride is suitable as the precipitant, provided that precautions are taken to prevent formation of the strongly basic secondary calcium phosphate. The method was originated by Bongartz[82] and later improved by Pfyl and Samter.[83]

Procedure: Dissolve a sample containing not more than 70 mg. of phosphorus pentoxide and neutralize to methyl yellow. Add 30 ml. of neutral

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[80] I. M. Kolthoff, *Chem. Weekblad*, **12**, 644 (1915).

[81] J. A. Calamari and R. Hubata, *Ind. Eng. Chem., Anal. Ed.*, **14**, 55 (1942).

[82] J. Bongartz, *Arch. Pharm.*, **22**, 846 (1884). See also W. M. Doherty, *Analyst*, **33**, 273 (1908).

[83] B. Pfyl, *Arb. kaiserl. Gesundh.*, **47**, 1 (1914); *Z. Untersuch. Nahr. u. Genussm.*, **43**, 313 (1922). B. Pfyl and W. Samter, *ibid.*, **48**, 325 (1924).

40% calcium chloride solution, heat to boiling in a resistant flask and cool to 14°C., then add phenolphthalein and titrate with carbonate-free alkali to a definite rose color, meanwhile shaking continually. Close the flask with a rubber stopper and allow to stand for two hours at 14°, after which the liquid will usually be colorless; then titrate further until the color returns. The error may amount to 1 or 2%. According to Tillmans and Bohrmann[84] titration may be made directly to the end-point without a period of standing. The method in any case cannot be recommended for exact analysis.

Damsgaard-Sörensen[85] and Tovborg-Jensen[86] determine phosphate as hydroxyapatite, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$. They prepare the sample in about 100 ml. of strongly acid solution, containing not more than 10 millimoles of phosphoric acid and 15 millimoles of calcium per liter, and neutralize with sodium hydroxide solution to a p_H of 4.7 (methyl red as indicator, with reference solution). Then 8 ml. of 0.5 M calcium chloride and 3 drops of 1% phenolphthalein are added and the solution is titrated with 0.1 N sodium hydroxide to a rose color. Upon boiling the mixture, the color returns to yellow and the precipitate coagulates; titration is continued until the phenolphthalein color will remain after two minutes of boiling. The reaction involved is:

$$6H_2PO_4^- + 10Ca^{++} + 14OH^- \rightarrow 3Ca_3(PO_4)_2 \cdot Ca(OH)_2 + 12H_2O$$

Results accurate to about 1% are obtained and the procedure takes little more than 5 minutes. Substances which consume alkali between the two end-points interfere. In the analysis of superphosphate, fluoride may be eliminated as hydrofluosilicic acid through evaporation with aqua regia. One dissolves 5 g. of superphosphate in 50 ml. of aqua regia (3 parts hydrochloric acid, sp. gr. 1.12, plus 1 part nitric acid, sp. gr. 1.25) at boiling, and evaporates not quite to dryness. The residue contains only 4–7% of the original fluoride, not enough to bother. In case evaporation is continued to dryness, an error possibly due to the formation of pyrophosphoric acid is encountered; therefore it is better to evaporate off only two-thirds of the liquid. The remainder is diluted to 250 ml. in a volumetric flask and is filtered, and a 20 ml. aliquot is neutralized to methyl red, barely acidified with 0.1 N hydrochloric acid, boiled to expel carbon dioxide, cooled, and brought to a p_H of 4.7 as described previously. Tovborg-Jensen obtained very good results in the analysis of samples so treated.

Fertilizers containing ammonium salts are first boiled for two hours in excess caustic soda to liberate the ammonia, then acidified with concentrated hydrochloric acid and boiled an hour longer, and finally diluted for analysis. Alternatively the ammonia may be oxidized to nitrogen by warming with excess bromine in alkaline solution (2 N sodium hydroxide) followed by addition of enough hydrochloric acid to make the solution 2 N and boiling to expel bromine. (It should be noted that large amounts of salts are undesirable during the neutralization, since the p_H of a monosodium phosphate solution is lowered in their presence; no account of this fact has been taken in the above procedure.)

Phosphoric Acid in the Presence of Calcium and Magnesium: In foods and other natural products, phosphoric acid usually occurs in the presence of calcium and magnesium. These cations are not disturbing in the titration as a monobasic acid but interfere in the determination as a dibasic acid because precipitates of varying composition are formed. The effect can be avoided by neutralizing first to methyl orange, adding an excess of neutral 10% potassium oxalate solution and finally titrating to a phenolphthalein end-point in the presence of salt (*cf.* p. 136) or to thymolphthalein. The accuracy is then the same as in the direct titration of phosphoric acid as a dibasic acid[87]; the procedure is well suited for determination of phosphate in food ash and for the rapid assay of calcium phosphate.

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[84] J. Tillmans and A. Bohrmann, *Z. Untersuch. Nahr. u. Genussm.*, **41,** 1 (1921). J. Tillmans, *ibid.*, **49,** 263 (1925).

[85] P. Damsgaard-Sörensen, *Kem. Maanedsblad,* **15,** 73 (1934).

[86] A. Tovborg-Jensen, *K. Veterin. Landsb. Aarskr.*, **1935,** p. 41.

Note: For the latter purpose a weighed sample is dissolved in a known excess of acid by boiling with a known amount of acid in resistant glassware. After cooling it is carefully neutralized to methyl orange with 0.1 N alkali, while being stirred thoroughly. The rest of the procedure in titrating to the second end-point is exactly as described on p. 136, except for addition of oxalate. From the difference between the two end-points the phosphate content is calculated; 1 ml. of 0.1 N alkali corresponds to 7.1 mg. of phosphorus pentoxide.

The amount of acid consumed in arriving at the methyl orange end-point indicates the quantity of calcium oxide present above that necessary to form primary phosphate, $Ca(H_2PO_4)_2$. By adding to this the amount present as primary phosphate (as calculated from the phosphate assay), the total calcium oxide may be found. In this way the ratio of calcium oxide to phosphorous pentoxide may be determined without the necessity of weighing the sample. One ml. of 0.1 N acid is equivalent to 2.8 mg. of calcium oxide. If the volume of acid consumed to methyl orange is equal to that of alkali taken between the end-points, the composition corresponds to secondary phosphate, $CaHPO_4$. A ratio of 2:1 in these volumes corresponds to tertiary phosphate, $Ca_3(PO_4)_2$.

Arsenic Acid and Arsonic Acids: The behavior of arsenic acid is similar to that of phosphoric acid. $K_1 = 5 \times 10^{-3}$, $K_2 = 8.3 \times 10^{-8}$.

King and Rutterford[88] have found that by titration to thymolphthalein in the presence of sufficient sodium chloride the following arsonic acids can be determined: methyl, phenyl, *p*-toluyl, *m*-xylyl, 3-nitro-*p*-toluyl, benzo, 3-nitrobenzo, 4-acetamido-3-benzo, 3-acetamido-4-benzo, and hippuroarsonic acid, as well as phenylarsonic acid disulfide.

Procedure: To about 0.1 g. of the acid, accurately weighed and dissolved in 20 ml. of water, add 2 drops of 0.1% thymolphthalein and titrate with 0.1 N sodium hydroxide to a pale blue color. Introduce an equal volume of saturated sodium chloride solution, previously neutralized to the same indicator, and complete the titration to blue.

Phosphorous Acid: $K_1 = 1.6 \times 10^{-2}$, $p_{K_1} = 1.8$
$K_2 = 7 \times 10^{-7}$, $p_{K_2} = 6.15$

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[87] I. M. Kolthoff, *Chem. Weekblad*, **13**, 910 (1916); *Pharm. Weekblad*, **52**, 1053 (1915). R. T. Thomson, *Z. anal. Chem.*, **24**, 232 (1885).

[88] H. King and G. V. Rutterford, *J. Chem. Soc.*, **133**, 2138 (1930).

In titration as a monobasic acid, methyl yellow, methyl orange, or bromophenol blue may be used as indicator. The titration exponent is about 3.9, but the end-point is not sharp and a reference solution is necessary. It is better to titrate as a dibasic acid to thymolphthalein, with which the change is more distinct.[89]

Hypophosphorous Acid, H_3PO_2: This compound behaves as a quite strong monobasic acid, the constant of which has a magnitude of about 3×10^{-2} but is influenced considerably by the concentration. Any indicator with a transition interval between those of methyl yellow and phenolphthalein may be employed in the titration.

Pyrophosphoric Acid:
$K_1 = 1.4 \times 10^{-1}, p_{K_1} = 0.85$
$K_2 = 1.1 \times 10^{-2}, p_{K_2} = 1.96$
$K_3 = 2.9 \times 10^{-7}, p_{K_3} = 6.54$
$K_4 = 3.6 \times 10^{-9}, p_{K_4} = 8.44$

The constants are such that titration is possible only as a dibasic or as a tetrabasic acid. The former is preferable; $p_T = \frac{1}{2}(p_{K_2} + p_{K_3}) = 4.25$. Long ago von Knorre[90] recommended methyl orange for titrations to the secondary salt. The change toward methyl yellow is at least as sharp as in the determination of phosphoric acid.[91] A 0.025 M solution of the secondary sodium salt has a p_H of 4.25, which changes to 3.6 upon the addition of 0.2 ml. of 0.1 N hydrochloric acid per 25 ml.

The fourth ionization constant of pyrophosphoric acid is so small that the acid cannot be titrated directly using phenolphthalein or even thymolphthalein. With the former the change to rose is very gradual and comes about 20% before the equivalence-point. An improvement is obtained by saturating the solution with sodium chloride or better by adding lithium chloride to a concentration of 20%. The end-point is still not sharp but can be located within an error of 1%.

Pyrophosphoric acid can be determined in the presence of ortho- and metaphosphoric acids by virtue of the fact that zinc pyrophosphate, in contrast with zinc orthophosphate, is only slightly soluble in weakly acid solution. According to Britske and Dragunov[92] the acid mixture is neutralized to bromophenol blue and treated with 2.5–3 times the theoretical requirement of zinc sulfate:

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[89] I. M. Kolthoff, *Rec. trav. chim.*, **46**, 350 (1927).

[90] G. von Knorre, *Z. angew. Chem.*, **5**, 639 (1892).

[91] I. M. Kolthoff, *Pharm. Weekblad*, **57**, 474 (1920).

[92] E. V. Britske and S. S. Dragunov, *J. Chem. Ind. (Moscow)*, **4**, 49 (1927); *Chem. Abstracts*, **22**, 2900 (1928). See also W. H. Koch, *Oil & Soap*, **21**, 175 (1944).

$$Na_2H_2P_2O_7 + 2ZnSO_4 \rightarrow Zn_2P_2O_7 + Na_2SO_4 + H_2SO_4$$

The free sulfuric acid is then titrated to the same color of the indicator. If metaphosphoric acid is present the titration must be made rapidly; otherwise it should be carried out slowly, especially at the end-point, at which the color should remain unchanged for 5 minutes. Larger amounts of the meta acid diminish the accuracy of the method.

In the presence of the precipitate the color change is not very sharp. Moreover, pure primary potassium orthophosphate when treated with zinc sulfate consumes a little alkali in the neutralization. For these reasons the method at best is not more accurate than to within 1.5%.[93]

Mixtures of Orthophosphoric and Pyrophosphoric Acids or Their Salts: (see also p. 143). The accurate determination of both of these acids in mixtures by means of acidimetric methods is not at all simple. The original procedure of von Knorre[90] was beset with several difficulties which, however, were corrected in a thorough investigation by Stollenwerk and Bäurle.[94] Their method is suitable for the determination of either acid alone or for both in a mixture. Interference would take place in the presence of meta- or polyphosphoric acids.

In the procedure one portion of the sample is hydrated by heating with nitric acid, the solution is neutralized to formation of primary alkali phosphate, and the total phosphate is titrated to formation of the tertiary salt. In this titration (A) each mole of H_3PO_4 consumes two equivalents of alkali and each mole of the original $H_4P_2O_7$ requires four equivalents. Another equal portion of sample is neutralized to the formation of $H_2PO_4^-$ and $H_2P_2O_7^{=}$, then treated with barium chloride and titrated with alkali to formation of the tertiary and quaternary salts, respectively:

$$2H_2PO_4^- + 3Ba^{++} \rightarrow Ba_3(PO_4)_2 + 4H^+$$
$$H_2P_2O_7^{=} + 2Ba^{++} \rightarrow Ba_2P_2O_7 + 2H^+$$

In this titration (B) one mole of either acid requires two equivalents of alkali. Expressing the titrations in milliequivalents (ml. of 1 N alkali), the calculations are made as follows:

$(B) - \frac{1}{2}(A)$ = millimoles of orthophosphoric acid or its salts
$\frac{1}{2}(A - B)$ = millimoles of pyrophosphoric acid or its

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[93] L. Sieg, *Dissertation*, Dresden 1931. H. Menzel and L. Sieg, *Z. Elektrochem.*, 38, 283 (1932).

[94] W. Stollenwerk and A. Bäurle, *Z. anal. Chem.*, **77**, 104 (1929).

Procedure: A weighed sample is dissolved in water, made to a known volume, and aliquot parts are taken for analysis.

(*A*). Acidify one portion with nitric acid (several ml. of concentrated) and keep for an hour or more just below boiling. Cool, neutralize to methyl orange (*cf.* p. 135) and complete the determination of total phosphate, either by precipitation of alkaline earth phosphate and titration of the liberated acid as previously described, or argentometrically by addition of sodium acetate and excess silver (p. 286).

(*B*). Titrate another equal volume with 0.1 N alkali, or with acid if the sample is a salt, to the methyl orange end-point. Precipitation with barium or calcium chloride can be made directly on this portion, but because of the presence of methyl orange Stollenwerk and Bäurle prefer to add the same amount of alkali to a fresh portion, without the use of methyl orange. Then introduce a three or fourfold excess of alkaline earth chloride in the cold, heat to boiling, and after cooling titrate with carbonate-free alkali to phenolphthalein, warm to 80°C., again cool, and complete the titration.

Note: This procedure (including the argentometric titration of total phosphate) has been tested and recommended by Sieg.[93] A thorough discussion of the combined acidimetric and argentometric method for the analysis of ortho-, meta-, and pyrophosphate mixtures is given by Gerber and Miles.[95] Instead of back-titrating excess silver, they determine the quantity of alkali necessary to neutralize the mixture in the presence of silver nitrate. Their procedure, for details of which the original articles should be consulted, represents a distinct improvement over the argentometric method of Aoyama.[96]

Determination of Ortho-, Meta- Pyro-, and Polyphosphates in Mixtures: On the basis of many experiments, Jones[97] developed new procedures for the separation and determination of the various phosphates. His investigations covered not only the ortho-, meta-, and pyro compounds, but also polyphosphates such as sodium tripolyphosphate, $Na_5P_3O_{10}$, and tetraphosphate, $Na_6P_4O_{13}$. Hexametaphosphate, $(NaPO_3)_6$, is precipitated with barium chloride in about 0.01 N hydrochloric acid solution. Trimetaphosphate is determined in the filtrate[98] after removal of other phosphates with barium chloride and alkali. In another portion the hexametaphosphate is separated as before, after which pyrophosphate is precipitated with manganous chloride at p_H 4.1 in the presence of a little acetone. Orthophosphate is separated as ammonium phosphomolybdate, after previous removal of any phosphates precipitated with barium chloride in a solution just acid to methyl red. The molybdate reaction is carried out rapidly to avoid interference from other phosphates. Polyphosphates are estimated by difference after determination of the total pentavalent phosphorus. In general the various isolated constituents are hydrolyzed to orthophosphate, which is precipitated as ammonium phosphomolybdate and titrated with sodium hydroxide (see p. 144).

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[95] A. B. Gerber and F. T. Miles, *Ind. Eng. Chem., Anal. Ed.*, **10**, 519 (1938); **13**, 406 (1941). See also A. Travers and Y. K. Chu, *Helv. Chim. Acta*, **16**, 913 (1933).

[96] S. Aoyama, *J. Pharm. Soc. Japan*, No. **520**, **7**, 533 (1925); *Bull. Imp. Hygienic Lab.*, **27**, 131 (1926); *Z. anal. Chem.*, **84**, 31 (1931). *Cf.* R. Dworzak and W. Reich-Rohrwig, *Z. anal. Chem.*, **77**, 14 (1929).

[97] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

[98] See also B. Wurzschmitt and W. Schuhknecht, *Angew. Chem.*, **52**, 711

Procedure: Prepare a solution of the sample in a volumetric flask, such that an aliquot portion of convenient size (25 or 50 ml.) will contain about 0.05 g. of total phosphorus pentoxide. The appropriate sample weight is chosen after a rough preliminary determination of the total as outlined below.

Conversion of Phosphates to Orthophosphoric Acid: Transfer an aliquot part of the solution to a beaker, bring to a volume of 75 to 100 ml., add 25 ml. of concentrated nitric acid, and boil gently for 15 minutes. Cool to room temperature and neutralize the excess acid with ammonium hydroxide so that the solution is just acid to litmus paper.

The total phosphorus pentoxide is determined on this portion by precipitation with 50 ml. of ammonium molybdate solution (p. 144) and titration of the washed precipitates with standard 1 N alkali. The other phosphate fractions after separation are treated similarly; 0.1 N alkali is used for titrating small quantities of precipitate.

Hexametaphosphate: Metaphosphate ions become hydrated rather quickly in solution, especially in strong acids or alkalies, so that this determination should be made promptly after preparation of the solution. Pipette into a beaker an aliquot portion of the same volume as was taken before and dilute, if necessary, to 50 ml. Add one drop of methyl orange (0.1%), barely acidify the solution with 1 N hydrochloric acid, and add 0.5 ml. in excess. Any free acid originally present should be neutralized before this step. While stirring, slowly add 15 ml. of barium chloride solution (25 g. $BaCl_2 \cdot 2H_2O$ per liter), then allow the precipitate to settle. If the solution becomes cloudy but no precipitate separates within a minute, stir vigorously for 15 second intervals until separation begins to take place as the stirring is stopped. Filter and wash the precipitate, first by decantation and finally four or five times on the paper, using small amounts of cold 0.1% barium chloride solution. Reserve the filtrate for determination of trimetaphosphate. Dissolve the precipitate in 1:1 nitric acid, convert to orthophosphoric acid and determine as ammonium phosphomolybdate.

Trimetaphosphate: To the filtrate reserved above add 1 N sodium hydroxide with stirring until the mixture remains definitely alkaline to phenolphthalein. Filter off the precipitated barium phosphates; trimetaphosphate alone remains in solution and is determined after conversion to ortho form.

Orthophosphate: Transfer an aliquot part of the original prepared solution to a beaker and bring to a volume of 100 ml. Barely acidify to methyl red with 1 N hydrochloric acid, add 25 ml. of barium chloride solution (25 g. $BaCl_2 \cdot 2H_2O$ per liter), and filter off any precipitate. Cool the filtrate to 20–25°C., add 8–10 g. of ammonium nitrate, and precipitate the orthophosphate with ammonium molybdate. Allow only 15 minutes for precipitation in order to minimize hydrolysis of other phosphates which would then interfere.

Pyrophosphate: Transfer an aliquot portion of freshly prepared solution to a beaker, make just acid to methyl orange with 1 N hydrochloric acid, and if hexametaphosphate is present add barium chloride in 10% excess over the stoichiometric requirement. Stir vigorously, filter off the precipitate, and dilute the filtrate to approximately 125 ml. Add 5 ml. of manganous chloride solution (100 g. $MnCl_2 \cdot 4H_2O$ per liter) and adjust the p_H of the solution to 4.1. This is done with the aid of a glass electrode or other suitable p_H meter, by adding 0.1 N sodium hydroxide dropwise with stirring. While continuing the stirring, add 7 or 8 ml. of acetone and allow the mixture to stand for 12–16 hours at 20–30°C. for precipitation of manganous pyrophosphate. Filter and wash with 0.1% manganous chloride solution, dissolve the precipitate in 1:1 nitric acid, and determine after conversion as before.

Polyphosphates: These are determined in terms of phosphorus pentoxide as the difference between total phosphorus pentoxide and the sum of the ortho-, meta-, and pyrophosphate equivalents.

While this calculation throws the accumulated errors on the polyphosphate value, the results are said to be sufficiently accurate for the classification of commercial products. More exact results may be obtained by resorting to gravimetric determinations of the orthophosphoric acid, but there are still some difficulties in the separation methods for which reference should be made to the original paper.

A qualitative test serves to indicate whether the poly compounds are present mainly as tripolyphosphate or as tetraphosphate. To the filtrate from a pyrophosphate determination one adds 25 ml. of barium chloride solution (2.5%); tetraphosphate gives a cloudiness or precipitate within 15 minutes, while tripolyphosphate shows no change.

Alkalimetric Determination of Phosphate as Ammonium Phosphomolybdate: Orthophosphates in cool or slightly warm dilute nitric acid solution yield with ammonium molybdate a yellow precipitate which under ideal conditions has the composition: $(NH_4)_3PO_4 \cdot 12MoO_3$. The precipitate reacts with alkali according to an equation represented more or less empirically as follows:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH \rightarrow 11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O$$

Procedure according to Jones[97]*:* Place the sample, which should contain orthophosphate equivalent to about 0.05 g. of phosphorus pentoxide, in a 250 ml. beaker. Dilute to 75 or 100 ml. and make just acid to methyl red with nitric acid. Add 50 ml. of ammonium molybdate reagent (see below) and allow to stand at room temperature for 15 minutes, or longer in the absence of interfering substances such as pyrophosphate. Filter and wash the precipitate with small amounts of 1% potassium nitrate solution cooled to 10–12°C., until 5 ml. of the washings requires less than 3 drops of 0.1 N sodium hydroxide to give a red color with phenolphthalein. Place the filter paper and precipitate in the original beaker and from a burette add sufficient 1 N sodium hydroxide to dissolve the ammonium phosphomolybdate and to give with phenolphthalein a red color which persists after stirring. Quickly titrate back just to colorless with 0.1 N hydrochloric acid and calculate the net volume of alkali consumed. Each milliliter of 1 N alkali is equivalent to 1.347 mg. of phosphorus or to 3.09 mg. of phosphorus pentoxide.

Ammonium Molybdate Reagent: Dissolve 100 g. of pure molybdic acid in a mixture of 400 ml. of cold distilled water and 80 ml. of ammonium hydroxide (sp. gr. 0.90). When completely dissolved, pour this slowly and with continuous stirring into a mixture of 400 ml. of nitric acid (sp. gr. 1.42) and 600 ml. of distilled water. Add 0.05 g. of sodium ammonium phosphate dissolved in a little water and stir. After 24 hours decant the clear solution through a filter paper into a reagent bottle. 60 ml. of this reagent suffices for 0.1 g. of phosphorus pentoxide.

Note: This volumetric determination appears to have been first studied by Pemberton in 1882, though he did not publish the details until eleven years later.[99] Meanwhile the method was described by Thilo,[100] who titrated with ammonium hydroxide, and by Hundeshagen.[101] Baxter[102] preferred to precipitate the phosphomolybdate in the reverse direction (phosphate added to molybdate) at room temperature or below. He then obtained a di- instead of a triammonium salt, requiring 24 equivalents of alkali per mole of phosphoric acid.

Several factors contribute to errors in the determination. The first is the difficulty of obtaining a precipitate of definite composition. Small amounts of phosphate do not precipitate readily at room temperature, whereas upon heating there is likelihood of occluding excess molybdic oxide. Hillebrand and Lundell[103] permit adding the molybdate reagent at 30–45°C. and allowing the mixture to stand for periods of from 15 minutes to 20 hours, though no further heating should be done after the addition of reagent. They suggest standardizing the alkali against a phosphate material of known composition, comparable with that being analyzed.

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[99] H. Pemberton, Jr., *J. Am. Chem. Soc.*, **15**, 382 (1893).

[100] E. Thilo, *Chem.-Ztg.*, **11**, 193 (1887).

[101] F. Hundeshagen, *Z. anal. Chem.*, **28**, 171 (1889).

[102] G. P. Baxter, *Am. Chem. J.*, **28**, 298 (1902). G. P. Baxter and R. C. Griffin, *ibid.*, **34**, 204 (1905).

[103] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis.* Wiley, New York 1929, pp. 562, 567.

The titration to phenolphthalein involves the objections that this indicator is not sufficiently sensitive to ammonium hydroxide and that it is sensitive to carbon dioxide. Still an indicator changing in the p_H range of phenolphthalein is required by the nature of other products present at the equivalence-point. It would be desirable to have more exact information concerning p_H values at and near the end-point. Although no pronounced p_H change is expected in this region, it might be possible to use a mixed indicator which would change at the optimum point. Neumann[104] sought to overcome the ammonia interference by boiling with excess alkali before titrating back. He then used a ratio of 28 equivalents per mole, but based this on a different molecular formula including free nitric acid. An alternative and probably better procedure for taking care of the ammonia is given on p. 156.

In general it may be said that the alkalimetric method is very useful for routine control purposes and that under carefully standardized conditions it is capable of giving quite accurate results. On the other hand, relatively large errors are possible if the proper conditions are not observed.

Sulfurous Acid: $K_1 = 1.7 \times 10^{-2}$, $p_{K_1} = 1.77$
$K_2 = 1.0 \times 10^{-7}$, $p_{K_2} = 7.00$

Sulfurous Acid as a Monobasic Acid: The titration exponent at the first equivalence-point is:

$$p_T = \tfrac{1}{2}(p_{K_1} + p_{K_2}) = 4.4$$

Therefore the solution may be titrated until completely alkaline to methyl yellow and the determination is quite satisfactory, especially if a reference solution of p_H 4.4 is used. Practical difficulties are presented by the volatility of sulfur dioxide and by rapid atmospheric oxidation, especially during the neutralization process. Sulfuric acid is formed and is titrated as a dibasic acid. To lessen the disturbance, alkali should be allowed to run in rapidly and when possible the solution should be overlain with nitrogen or other inert gas.

Sulfurous Acid as a Dibasic Acid: As the table on p. 113 shows, an acid whose constant is 10^{-7} cannot be titrated exactly in 0.1 N solution with phenolphthalein as indicator. Although this titration has been recommended in the literature, the end-point is gradual and occurs 5 or 6% too soon. Addition of sodium chloride helps; if the solution is saturated with this salt at the end-point, results accurate to within 1% can be obtained.[105] One may also remove the sulfite ions by precipitation with barium.

Procedure: The solution is titrated with alkali until red to phenolphthalein, then an excess of 10% barium chloride is added, and titration is continued until the color returns to a pale rose.

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[104] A. Neumann, *Z. anal. Chem.*, **42**, 792 (1903).

[105] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **109**, 69 (1920).

Sulfurous acid may also be titrated using thymolphthalein as indicator, without any salt. Carbonate-free alkali is added until a pale blue color appears. Täufel and Wagner[106] obtained good results in this way.

Use can also be made of the complex formation between sulfite and mercuric ions:

$$2HSO_3^- + Hg^{++} \rightarrow Hg(SO_3)_2^{=} + 2H^+$$

whereby sulfurous acid may be titrated as a dibasic acid with methyl yellow as indicator.[107]

Procedure: To about 25 ml. of 0.05 M sulfurous acid (or 0.1 M bisulfite) add 25 ml. of 0.1 M mercuric chloride or its equivalent of a stronger solution and neutralize with alkali to methyl yellow. The accuracy is about 1%.

Chromic Acid: In its first dissociation step, chromic acid behaves as a strong acid; the first constant is quite large. The second constant is much smaller, about 3.2×10^{-7}, and titration as either a monobasic or a dibasic acid is possible.

Chromic Acid as a Monobasic Acid:

$$H_2CrO_4 + OH^- \rightleftarrows HCrO_4^- + H_2O$$
$$2HCrO_4^- \rightleftarrows Cr_2O_7^{=} + H_2O$$

Most of the acid-chromate ions combine to form the so-called "dichromate ions," the equilibrium constant for this reaction being given[108] by the expression:

$$\frac{[HCrO_4^-]^2}{[Cr_2O_7^{=}]} = 2.3 \times 10^{-2}$$

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[106] K. Täufel and C. Wagner, *Z. anal. Chem.*, 68, 25 (1926).

[107] Unpublished experiments of I. M. Kolthoff. See also E. Bosshard and W. Grob, *Chem.-Ztg.*, 37, 465 (1913); A. Sander, *ibid.*, 39, 945 (1915).

Thiosulfate also reacts with mercuric chloride:

$$2Na_2S_2O_3 + 3HgCl_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4HCl + (2HgS)\cdot HgCl_2$$

The free acid can be determined with sodium hydroxide. *Cf.* A. Wöber, *Chem.-Ztg.*, **41**, 569 (1917); **44**, 601 (1920); J. Bodnár, *Z. anal. Chem.*, **53**, 37 (1914); **55**, 209 (1916); A. Sander, *Z. angew. Chem.*, **28**, 9 (1915); **29**, 11 (1916). Bodnár noted that silver thiosulfate decomposes rapidly according to the equation:

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$$

and he made an analytical application of the reaction by titrating the sulfuric acid.

[108] J. D. Neuss and W. Rieman III, *J. Am. Chem. Soc.*, **56**, 2238 (1934).

In practice the equivalence-point is reached at a p_H of about 4, therefore methyl yellow, methyl orange, or bromophenol blue might be employed as indicators. The determination is not exact because of interference by the dichromate color. On this account a reference solution of pure potassium dichromate should be used with the same amount of indicator as in the analysis, and larger quantities of indicator than those ordinarily taken are to be recommended. Because of the color disturbance, the error generally exceeds 1%.

A more suitable indicator is tri(2,4-dimethoxyphenyl) carbinol, which is red-violet in acid solution and colorless in alkaline. The transition interval lies between 2.8 (red) and 4.0 (colorless). A dichromate comparison solution is essential in this case also.

Chromic Acid as a Dibasic Acid: Here again the second ionization constant is too small to permit the accurate titration of 0.1 N solution with phenolphthalein as indicator (see table, p. 113). According to Richter[109] the determination should give good results, but Kolthoff and Vogelenzang[110] found the change coming somewhat too early. They obtained serviceable results with thymolphthalein, taking the end-point as a green color rather than a blue because of the effect of chromate.

Phenolphthalein may be used if at the end-point the solution is approximately saturated with sodium chloride (*cf.* under sulfurous acid). Another procedure consists in removing the chromate ions with barium chloride. The barium salt should be added only toward the end of the titration when the phenolphthalein color has already appeared, otherwise a barium acid chromate is precipitated. Too little alkali is then used and the error may be serious.

The titration of chromic acid is tedious since the neutralization process goes so slowly. If 0.1 N solutions are employed, phenolphthalein shows a fading red color 40% in advance of the equivalence-point. The phenomena are similar to those noted with carbonic acid. One must titrate until the color remains even after standing for 5 minutes. The neutralization takes place more quickly in more dilute solutions, an observation which may be explained by assuming that dichromate ion reacts slowly:

$$Cr_2O_7^{=} + H_2O \rightleftarrows 2HCrO_4^{-} \quad (1)$$

$$Cr_2O_7^{=} + 2OH^{-} \rightleftarrows 2CrO_4^{=} + H_2O \quad (2)$$

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[109] M. Richter, *Z. anal. Chem.*, **21**, 204 (1882).

[110] I. M. Kolthoff and E. H. Vogelenzang, *Rec. trav. chim.*, **40**, 681 (1921).

whereas, on the other hand, the neutralization of $HCrO_4^-$ is instantaneous. With increasing dilution, the equilibrium in reaction (1) is shifted to the right and the rate of neutralization is increased correspondingly.

Mercapto Acids: From determination of the ionization constants, Larsson[111] was able to calculate and to confirm experimentally that of the aliphatic mercapto acids only α-mercaptoisobutyric and thiomalic acids can be titrated well to phenolphthalein (p_T = 8.0–8.4). For thioglycolic and α- or β-thiolactic acids, phenol red or neutral red is more suitable (p_T = 7.4 ± 0.2), while for β-thiomalamidic acid, bromothymol blue should be used (p_T = 6.7).

Acid	p_{K_1}	p_{K_2}
Thioglycolic	3.67	10.67
α-Thiolactic	3.69	10.70
β-Thiolactic	4.34	10.54
α-Mercaptoisobutyric	3.90	11.32
β-Thiomalamidic	3.5	9.9
Thiomalic (p_{K_3} = 11.2)	3.28	4.9

Nothing need be said here about the polyacid bases. Details concerning the more important diacid alkaloids are given on page 127.

6. Titration of Two Acids or Two Bases in the Presence of Each Other.—These cases are related to those already discussed, of polybasic acids or polyacid bases; the theory has been outlined in Vol. I, pp. 26, 56. If the correct titration exponent can be attained to within 0.2 in p_H, and if the ratio of the two ionization constants is greater than 10,000, the determination may be accurate to within 0.5%. The titration exponent sought is given by the expression:

$$p_T = \tfrac{1}{2}(p_{K_1} + p_{K_2})$$

when the two acids are present in equivalent concentrations. If the concentration ratio of the stronger acid to the weaker is r, the titration exponent becomes:

$$p_T = \tfrac{1}{2}(p_{K_1} + p_{K_2}) + \tfrac{1}{2}\log r$$

With the aid of equations given in Vol. I, p. 30, the changes in p_H near the first equivalence-point may be calculated for a given case. As an example, consider the titration of 25 ml. of 0.1 N acetic acid (p_K = 4.74) in the presence of 25 ml. of 0.1 N boric acid (p_K = 9.22).

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[111] E. Larsson, *Z. anal. Chem.*, **79**, 170 (1929); *Ber.*, **B63**, **1347** (**1930**).

p_H = 6.64 (1% before the equivalence-point)
p_H = 6.99 (at the equivalence-point, p_T)
p_H = 7.34 (1% after the equivalence-point)

With a reference solution of $p_H = 7.0$ and using phenol red, neutral red, or a mixed indicator, the acetic acid may be titrated easily to within 0.5%. The reference liquid may be a buffer mixture or, more simply and just as exactly, a solution of 25 ml. of 0.1 N sodium acetate, 25 ml. of 0.1 N boric acid, 25 ml. of water, and indicator. This has the same composition as the titrated sample at the first equivalence-point. Since a deviation of 5% in either solution has scarcely any effect on the p_H, the solutions need not be prepared very carefully.

In the way that had been described it is possible to titrate to within 0.5% the following acids in the presence of boric acid: oxalic, tartaric, citric, formic, lactic, benzoic, and salicylic. In each case the correct p_T is indicated by an appropriate comparison solution.[112]

The titration of phosphoric acid in the presence of boric is much less favorable because the ratio of K_2 (phosphoric) to K (boric) is only about 300. The best results, which may be in error by 2 or 3%, are obtained at the first rose color of phenolphthalein.

The acids which have been mentioned may be determined even more sharply in the presence of phenol than in the presence of boric acid, since phenol has a smaller ionization constant. In the case of phosphoric acid the error is about 1% if a p_T of 8.0 is attained.

The determination of ammonia ($p_K = 4.76$) in the presence of pyridine ($p_K = 8.90$) is of practical importance since by-product ammonia may contain pyridine as an impurity.

$$p_T = 14.2 - \tfrac{1}{2}(p_{K_1} + p_{K_2}) = 7.35 \text{ (at 15°C.)}$$

In this case, therefore, one uses a reference solution of $p_H = 7.35$, with neutral red or phenol red as indicator. For example, mixtures of 25 ml. each of 0.1 N ammonia and 0.1 N pyridine were titrated with 0.1 N hydrochloric acid. A reference solution was prepared from 25 ml. each of 0.1 N ammonium chloride, 0.1 N pyridine, and water. The end-points could be recognized to within 0.1 ml., and three titrations required 25.0, 24.95, and 24.97 ml. of 0.1 N acid.

The determination of ammonia in the presence of hexamethylenetetramine will be considered later (p. 217).

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[112] I. M. Kolthoff, *Pharm. Weekbl.*, **59**, 129 (1922). See also H. T. Tizard and A. R. Boeree, *J. Chem. Soc.*, **119**, 132 (1921).

CHAPTER V

ACID-BASE DISPLACEMENT TITRATIONS

1. Accuracy of Titrations Involving Weak Acid Displacement.—In displacement reactions the base that is bound to a weak or slightly soluble acid is titrated with a stronger acid which replaces the weaker. Conversely, the acid that is held by a weak base may be titrated with a stronger base.

The table on p. 151 has been prepared to show the accuracy that may be expected in determinations of this sort under various conditions. Values are given for the titration exponent p_T ($p_T = p_H$ at equivalence-point, where the weak acid has been quantitatively displaced) and for the p_H just before and after the equivalence-point, to show the magnitude of changes occurring with solutions of different concentrations. In calculating these p_H values, the ionization of the weak acid has naturally been considered. When the acid is only slightly soluble the case is more complicated because the ion product must then be taken into account. Some of these special cases will be considered separately.

Titration of 0.01 N Solutions: Bound alkali may be titrated without a reference solution provided that the ionization constant of the acid displaced is less than 5×10^{-9}. Methyl red and chlorophenol red are the best indicators. Using a comparison solution of the proper p_H, the titration can be accurate to within 0.2% if K_a is below 5×10^{-8}. In this way one can satisfactorily determine arsenites ($p_{K_a} = 9.22$), borates ($p_{K_a} = 9.18$), cyanides ($p_{K_a} = 9.14$), and salts of veronal ($p_{K_a} = 7.43$) in 0.01 N solution. A study of the microdetermination of carbonate with 0.01 N hydrochloric acid and methyl red as indicator was made by Mika,[1] who titrated to a p_T of 5.0 and applied an experimentally observed indicator correction.

Titration of 0.1 N Solutions: If the values of K_a are less than 5×10^{-8}, 0.1 N solutions may be titrated with an accuracy of 0.2%, best with methyl red as indicator. Using a comparison solution, the same accuracy may be obtained with acids of $K_a = 5 \times 10^{-7}$, which include carbonic acid. Because the carbon dioxide liberated in this case produces a somewhat acid reaction at the equivalence-point, it is desirable that the reference solution be saturated with carbon dioxide and contain the same amount of neutral salt as the titrated solution.

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[1] J. Mika, *Z. anal. Chem.*, **101**, 270 (1935).

TITRATION EXPONENT AND p_H CHANGE NEAR THE EQUIVALENCE-POINT IN DISPLACEMENT OF A WEAK ACID

K_a	p_H, 1% before p_T	p_H, 0.2% before p_T	p_T	p_H, 0.2% after p_T	p_H, 1% after p_T
	1 N Solutions				
10^{-3}	1.70		1.66		1.60
10^{-4}	2.30	2.18	2.15	2.12	2.00
10^{-5}	3.07	2.75	2.65	2.55	2.22
10^{-6}		3.45	3.15	2.87	2.29
10^{-7}		4.30	3.65	2.98	2.30
10^{-8}		5.30	4.15	3.00	2.30
10^{-9}		6.30	4.65	3.00	2.30
	0.1 N Solutions				
10^{-3}	2.20		2.19		2.17
10^{-4}	2.70		2.66		2.60
10^{-5}	3.30	3.19	3.16	3.13	3.00
10^{-6}	4.07	3.75	3.65	3.55	3.22
10^{-7}		4.45	4.15	3.87	3.29
10^{-8}		5.30	4.65	4.00	3.30
10^{-9}		6.30	5.15	4.00	3.30
	0.01 N Solutions				
10^{-3}	2.75		2.75		2.76
10^{-4}	3.20		3.19		3.17
10^{-5}	3.70		3.66		3.60
10^{-6}	4.30	4.19	4.16	4.13	4.00
10^{-7}	5.07	4.75	4.65	4.55	4.22
10^{-9}		5.45	5.15	4.87	4.29
10^{-9}		6.30	5.65	5.00	4.30

Salts of polybasic acids may be titrated to the formation of acid salts, the same conditions applying as were established for determinations of the free acids (p. 113). Thus phosphates and glycerophosphates in 0.1 N solution are titratable to primary salts, and pyrophosphates to the secondary salts, using methyl orange. Application of the phosphate titration can be made to the determination of magnesium or of phosphate, these ions being precipitated as magnesium ammonium phosphate, filtered, washed first with a little water and then with alcohol, and finally being dissolved in an excess of standard acid which is titrated back.[2]

Titration of 1 N Solutions: At this concentration, titrations having an accuracy of 0.2% may be extended without a comparison solution to salts of acids with K_a values up to 5×10^{-7}, or up to 5×10^{-6} with one; thymol blue and tropeolin OO are the most suitable indicators. If an error of 1% is permissible, salts whose acid constants are 10^{-4} or less may be determined.

This fact has a practical use in the rapid estimation of acetates. The ionization constant of acetic acid is 1.75×10^{-5} ($p_K = 4.76$); in the titration of 1 N acetate with 1 N hydrochloric acid the p_T is 2.53. It is best to use for comparison a solution about 0.5 N in acetic acid and 0.5 N in sodium chloride, but freshly prepared 0.003 N hydrochloric acid is also satisfactory. In the analysis of alkaline earth acetates it is appropriate to substitute alkaline earth chloride for the sodium chloride. With tropeolin OO or thymol blue as indicator the determination of acetate in 1 N solution may be made with 0.2% accuracy in this way.[3]

Propionates, butyrates, valerianates, and succinates may be determined in the same manner.

The ionization constant of formic acid is too large ($K_a = 1.77 \times 10^{-4}$, $p_K = 3.75$) to allow exact titration of formates by displacement. In dealing with 1 N solutions and using 0.5 N formic acid or 0.01 N hydrochloric acid for reference, the error may be kept below 2%.

When benzoates are titrated with acid, benzoic acid separates as a thick paste in which no color change can be recognized even though the ionization constant is fairly small ($K_a = 6.86 \times 10^{-5}$, $p_K = 4.16$). Therefore the free acid should be removed by dissolving in ether. To 25 ml. of 1 N benzoate one adds 0.5 ml. of thymol blue indicator and 25 ml. of ether. As a comparison mixture 50 ml. of water is taken with 25 ml. of ether and the appropriate quantities of benzoic acid, sodium chloride, and indicator. During the titration, which is preferably carried out in a glass-stoppered bottle or flask, the mixture is shaken vigorously and near the equivalence-point one waits between additions until the lower layer becomes clear. The end-point may be perceived within about 1%.

Salicylates may be titrated in the same way as benzoates. Although K_a is quite large, 1.06×10^{-3}, the acid liberated does not interfere seriously because it is nearly all extracted.

Citrates and tartrates cannot be determined by simple displacement methods because of the high values of their first ionization constants. Whether or not salts of other particular acids may be titrated exactly can generally be decided on the basis of data in the table on p. 151.

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[2] F. Hundeshagen, *Chem.-Ztg.*, **18**, 445 (1894). *Cf.* H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig 1913, p. 167.

[3] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **115**, 168 (1921).

Displacement Titrations in the Presence of Acetone: From investigations of Pring[4] and of Cray and Westrip[5] it appears that the ionization constants—in the Brönsted sense—of organic cation acids (anilinium, pyridinium, etc.) are slightly increased if 90% acetone is substituted for water as a solvent. On the other hand, the ionization constants of carboxylic acids are greatly decreased; the p_{K_1} values rise by 4 or 5 units and the p_{K_2} values by about 6 units. There is little effect on the dissociation of strong acids like hydrochloric or perchloric. Because the ion product of water is decreased (to about $10^{-19.7}$) there is a much greater p_H change when a strong acid is titrated with a strong base in 90% acetone than in water.

Richardson[6] made use of these facts in the displacement titrations of salts of organic acids with stronger acids. If one employs an alkali-sensitive basic indicator of the methyl yellow type, whose indicator constant is only slightly different in 90% acetone from that in water, a pronounced color change marks the end-point. Linderström-Lang[7] used benzeneazo-α-naphthylamine (α-naphthyl red) while Richardson recommended *p*-benzenesulfonic acid azo-α-naphthylamine (naphthylamine orange). In some cases neutral red and erythrosin were found useful.

Richardson was able to titrate acetates, lactates, citrates, and even oxalates. The salts are dissolved in as little water as possible and are diluted with ten times as much acetone (it is a practical disadvantage that most salts are not very soluble in this medium). From a microburette one adds 0.05 N hydrochloric acid in 75% alcohol, this solvent being chosen for the standard solution rather than acetone which is too volatile. Two drops of 0.1% naphthylamine orange in 75% alcohol are used per 10 ml. of solution and the end-point is obtained by comparison with reference standards in 90% acetone: (*a*) 0.0004 N hydrochloric acid and indicator, orange-red at a p_H of 3.4 (*b*) a mixture 0.05 M in pyridine and pyridine hydrochloride with indicator, orange-yellow at a p_H of about 4.0. One can also apply an indicator correction in the ordinary way.

2. Accuracy of Titrations Involving Weak Base Displacement.—A table giving the p_H changes near the equivalence-point serves again here to demonstrate the accuracy with which a strong acid bound to a weak base may be titrated. The calculations apply at 22°C. ($K_w = 10^{-14}$); at 15° all the p_H values would be raised by 0.2 unit.

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[4] J. N. Pring, *Trans. Faraday Soc.*, **19**, 705 (1923).

[5] F. M. Cray and G. M. Westrip, *Trans. Faraday Soc.*, **21**, 326 (1925).

[6] G. M. Richardson, *Proc. Roy. Soc. London*, **B115**, 121, 142, 170 (1934).

[7] K. Linderström-Lang, *Z. physiol. Chem.*, **173**, 32 (1928).

TITRATION EXPONENT AND p_H CHANGE NEAR THE EQUIVALENCE-POINT IN DISPLACEMENT OF A WEAK BASE

K_b	1 N Solutions				
	p_H, 1% before p_T	p_H, 0.2% before p_T	p_T	p_H, 0.2% after p_T	p_H, 1% after p_T
10^{-3}	12.30		12.35		12.40
10^{-4}	11.70	11.82	11.85	11.88	12.00
10^{-5}	10.93	11.25	11.35	11.45	11.78
10^{-6}		10.55	10.85	11.13	11.71
10^{-7}		9.70	10.35	11.02	11.70
10^{-8}		8.70	9.85	11.00	11.70
10^{-9}		7.70	9.35	11.00	11.70
	0.1 N Solutions				
10^{-3}	11.80		11.81		11.83
10^{-4}	11.30	11.33	11.34	11.36	11.40
10^{-5}	10.70	10.81	10.84	10.87	11.00
10^{-6}	9.93	10.25	10.35	10.45	10.78
10^{-7}		9.55	9.85	10.13	10.71
10^{-8}		8.70	9.35	10.00	10.70
10^{-9}		7.70	8.85	10.00	10.70
	0.01 N Solutions				
10^{-3}	11.25		11.25		11.25
10^{-4}	10.80		10.81		10.83
10^{-5}	10.30		10.34		10.40
10^{-6}	9.70	9.81	9.84	9.87	10.00
10^{-7}	8.93	9.25	9.35	9.45	9.78
10^{-8}		8.55	8.85	9.13	9.71
10^{-9}		7.70	8.35	9.00	9.70

Titration of 0.01 N Solutions: In the presence of phenolphthalein as indicator, strong acids may be determined with an accuracy of 0.2% if they are combined with bases of ionization constants below 5×10^{-9}. Salts of aniline and of pyridine are included in this group. With the aid of a reference solution the constants should be 5×10^{-8} or less for the same accuracy to be attained; thymol blue or phenolphthalein serves as indicator. The alkali used must of course be carbonate-free.

Titration of 0.1 N Solutions: A bound acid may be determined within 0.2% using phenolphthalein, thymol blue, or thymolphthalein without a comparison solution, if K_b is below 5×10^{-8}. With a standard for reference, constants of up to 5×10^{-7} may be included with the same accuracy. Thymolphthalein is a suitable indicator, as in the titration of salts of nicotine ($K_b = 7 \times 10^{-7}$).

Titration of 1 N Solutions: Accuracy of 0.2% is possible in the case of normal solutions if K_b is less than 10^{-7} or if K_b is less than 10^{-6} and a comparison solution is used. Thymolphthalein, nitramine, tropeolin O, and alizarin yellow are satisfactory indicators. A practical application may be made to the rapid analysis of ammonium salts ($K_b = 1.75 \times 10^{-5}$). By employing a 0.2 M solution of sodium carbonate for reference and tropeolin O as indicator, the titration with 1 N alkali is accurate to within 1%. The method is also useful for the titration of hydrazine salts ($K_b = 3 \times 10^{-6}$).

3. Special Displacement Methods; Titrations in the Presence of Alcohol and Formaldehyde.—Alcohol has the property of strongly lowering the ionization constants of the nitrogen bases. This effect makes possible a determination of the acid components of salts of fairly strong bases, which could not be carried out in aqueous solutions. Since the constants of the various bases and indicators in alcohol mixtures are not yet well enough known, theoretical treatment of the titration errors will be omitted and only some practical details given.

Ammonium Salts: Vorländer[8] established that in strongly alcoholic solutions certain amines no longer react alkaline to phenolphthalein; this fact was utilized by Willstätter and Waldschmidt-Leitz[9] for a rapid analysis of ammonium salts. In their procedure the alcohol content must amount to at least 97% at the end of the titration, but the authors have found concentrations of 90% satisfactory, while according to Foreman[10] as little as 80% is sufficient. Lövgren[11] in a thorough study obtained very good results with 50% alcohol at the end-point, using thymolphthalein as indicator. The final volume, however, should not be much more than 10 ml.

Phosphate: Greta Hammarsten[12] made use of the fact that ammonia in the presence of much acetone no longer reacts alkaline to thymolphthalein for a determination of phosphate in ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot HNO_3$. The washed precipitate (see p. 144) is dissolved in 3–5 ml. of 1 N ammonium hydroxide and the filter is rinsed with 15–20 ml. of carbon dioxide-free water. The solution is treated with 55 ml. of acetone and 1 ml. of 0.5% thymolphthalein in alcohol and is titrated to a blue color with 1 N potassium hydroxide in 90% alcohol. A blank test is carried out with 25 ml. of water, 50 ml. of acetone, and 1 ml. of indicator. Each millimole of phosphorus corresponds to 28 milliequivalents of alkali, but an empirical factor of 1.12 mg. of phosphorus per ml. of 1 N alkali gives better results when more than 2 mg. is present. The accuracy is about 1%; by substituting 10 ml. of formaldehyde for the 55 ml. of acetone one obtains equally useful values.

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[8] D. Vorländer, *Ann.*, **341**, 76 (1905); *Ber.*, **52**, 309 (1919).

[9] R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **54**, 2988 (1921); *Z. physiol. Chem.*, **132**, 194 (1924).

[10] F. W. Foreman, *Biochem. J.*, **14**, 451 (1920).

[11] S. Lövgren, *Z. anal. Chem.*, **64**, 457 (1924).

[12] G. Hammarsten, *Compt. rend. trav. lab. Carlsberg*, **17**, No. 5 (1927); *Chem. Abstracts*, **22**, 1302 (1928).

Hydrazine Salts: Hydrazine may be titrated sharply to methyl red as a monoacid base (formation of $N_2H_4 \cdot HCl$), its second ionization constant being very small. According to Stempel,[13] hydrazine reacts with formaldehyde to form a compound that is not alkaline to phenolphthalein. Therefore the acid component of a hydrazine salt can be liberated by addition of formaldehyde and titrated as described for ammonium salts (*cf.* above and p. 158).

Alkali Nitrites: Stempel[14] applied the formol titration of hydrazine to the determination of alkali nitrites. If one adds excess hydrazine sulfate to a nitrite, the following reaction occurs:

$$NaNO_2 + N_2H_4H_2SO_4 \rightarrow NaNH_4SO_4 + N_2O + H_2O$$

In the formol titration each mole of hydrazine sulfate remaining requires two equivalents of alkali, while a mole of the sodium ammonium salt requires only one.

Procedure: To 40 ml. of 0.05 M hydrazine sulfate solution add 20 ml. of about 0.05 M nitrite solution (neutral to neutral red) and warm for 20 minutes on a water bath. After cooling add 15 ml. of neutral formaldehyde and titrate with 0.1 N alkali to phenolphthalein. Run a blank on the same quantity of hydrazine sulfate solution and from the difference between the amounts of alkali consumed calculate the nitrite content of the sample. 1 ml. of 0.1 N alkali corresponds to 6.9 mg. $NaNO_2$ or 8.51 mg. KNO_2.

Amino Acids and Polypeptides: In the classical view, addition of alkali to an amino acid neutralizes the carboxyl group:

$$NH_2RCOOH + OH^- \rightarrow NH_2RCOO^- + H_2O$$

whereas according to Bjerrum[15] the amino acids exist in solution as dipolar (amphoteric) ions which upon addition of hydroxyl ions are converted to anion bases:

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[13] B. Stempel, *Z. anal. Chem.*, **91,** 412 (1933).

[14] B. Stempel, *Z. anal. Chem.*, **91,** 413 (1933).

[15] N. Bjerrum, *Z. physik. Chem.*, **104,** 147 (1923). For a summary, see I. M. Kolthoff, *Acid-Base Indicators*, translated by C. Rosenblum, Macmillan, New York 1937, pp. 42–47.

$$^{+}NH_3RCOO^- + OH^- \rightarrow NH_2RCOO^- + H_2O$$

The ionization constant of such a free base is fairly large (around 10^{-4}) so that in aqueous solution scarcely any alkali is required to redden phenolphthalein. Birckner[16] observed that alcohol increases the acid character of amino acids, while Foreman[10] independently developed methods for the titration of these acids and of ammonium salts in the presence of alcohol or acetone (or of formaldehyde, see p. 158). Mos tamino acids may be titrated quantitatively in 97% alcohol with phenolphthalein as indicator; the procedure is much the same as for ammonium salts (p. 155), under which literature references are given.[17] With thymolphthalein less alcohol is required.

The basic groups of polypeptides are much weaker than those of amino acids. Because of this, the polypeptides may be titrated in 40–50% alcohol to phenolphthalein. It must be remembered that under these conditions the simple amino acids also consume alkali, to about 28% of the theoretical amount. These facts find application in the analysis of mixtures of amino acids and polypeptides. Willstätter and Waldschmidt-Leitz[18] determine the sum of the two by titration in 97% alcohol (b ml. required), then titrate an equal portion in 50% alcohol (a ml. required). Letting x represent the amount of alkali used by the amino acids in 97% alcohol, so that $(b - x)$ equals that used by the polypeptides, it follows from the foregoing that:

$$x = \frac{100(b - a)}{72}$$

When the true ionization constant of the basic group is large, as in the case of lysine ($K_b = 10^{-1.9}$) or aspartic acid ($K_b = 10^{-1.8}$), no good results can be expected from titrations to phenolphthalein, even in the presence of alcohol. Taking aspartic acid as an illustration, it was shown by Foreman that carboxyl group I*a* can be neutralized accurately, but not group I*b*. One can consider that after neutralization of group I*a* the molecule exists as a dipolar ion of composition II:

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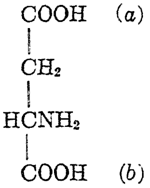
[16] V. Birckner, *J. Biol. Chem.*, **38**, 245 (1919).

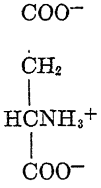
[17] See also E. L. Tague, *J. Am. Chem. Soc.*, **42**, 173 (1920); S. L. Jodidi, *ibid.*, **40**, 1031 (1918); and L. J. Harris, *J. Chem. Soc.*, **123**, 3294 (1923); *Proc. Roy. Soc. London*, **B95**, 440, 500 (1923); **B97**, 364 (1925).

[18] R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **54**, 2988 (1921). See also E. Takamiya, *Bull. Agr. Chem. Soc. Japan*, **3**, 66 (1927); *Chem. Abstracts*, **22**, 743 (1928).



$$\begin{array}{l}\mathrm{COOH}\quad (a)\\ \ \ |\\ \mathrm{CH_2}\\ \ \ |\\ \mathrm{HCNH_2}\\ \ \ |\\ \mathrm{COOH}\quad (b)\end{array}$$

I



$$\begin{array}{l}\mathrm{COO^-}\\ \ \ |\\ \mathrm{CH_2}\\ \ \ |\\ \mathrm{HCNH_3^+}\\ \ \ |\\ \mathrm{COO^-}\end{array}$$

II

The basic group having such a high ionization constant, it cannot be displaced quantitatively by another strong base. In certain cases, with alanine or tyrosine, for instance, the titration is possible according to Harris[19] with thymolphthalein as indicator; improvement can also be brought about by heating the solution.

With the aid of Bjerrum's amphoteric ion theory it is possible to account for the behavior of widely different amino acids in the titration with alkali.

Function of Formaldehyde in the Titration of Ammonium Salts and Amino Acids:

Ammonium Salts: Formaldehyde combines with ammonia to form hexamethylenetetramine. This compound is such a weak base ($K_b = 8 \times 10^{-10}$) that its aqueous solution does not react alkaline to phenolphthalein. Therefore ammonium salts in the presence of formaldehyde may be titrated sharply even in dilute solution, using this indicator. The reaction with formaldehyde proceeds rapidly enough to permit direct titration with alkali.[20]

Procedure: To 25 ml. of about 0.1 M ammonium salt solution add 5 ml. of 37% formaldehyde which has previously been neutralized to phenolphthalein, and add 0.1 ml. of a 1% solution of this indicator. Allow to stand for one minute, then titrate with 0.1 N alkali to a faint pink. Each milliliter corresponds to 1.804 mg. ammonium ion. The determination also gives good results with 0.01 N solution, using carbonate-free alkali.

Note: If the ammonium salt solution contains an excess of acid or base, it should first be neutralized. When only anions of strong acids are present, this may be done conveniently toward methyl red. In the presence of anions of weak acids neutral red or phenol red is preferable (see p. 149). The ammonium content of an ammonium acetate solution may be determined rapidly in this way.

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[19] L. J. Harris, *Proc. Roy. Soc. London*, **B95**, 440, 500 (1923).

[20] I. M. Kolthoff, *Pharm. Weekblad*, **58**, 1463 (1921).

Amino Acids: The method of Sörensen[21] for the alkalimetric determination of amino acids in the presence of formaldehyde is widely used in physiological chemistry. Formaldehyde reacts with amino groups to form very weak "Schiff's bases":[22]

$$RNH_2 + O{=}CH_2 \rightleftarrows RN{=}CH_2 + H_2O$$

Qualitatively, therefore, formaldehyde produces the same effect on amino acids as does alcohol or acetone. However, whereas alcohol and acetone lower the ionization constant of a basic group by changing the solvent, formaldehyde brings about the formation of a much weaker base. According to modern views, the amino group $-NH_2$ is first liberated from a dipolar ion by addition of alkali:

$$^+NH_3RCOO^- + OH^- \rightleftarrows NH_2RCOO^- + H_2O$$

after which the free base and aldehyde combine:

$$NH_2RCOO^- + CH_2O \rightleftarrows H_2CNRCOO^- + H_2O$$

In this way the hydroxyl-ion concentration that would arise from the free base is strongly repressed. From the measurements of Harris[23] it appears that the ionization constant of the methylene derivative is about 10^{-3} times that of the original amino group. To determine the value exactly, the equilibrium between the two forms would have to be considered.

Harris[24] later studied the quantitative side of the question more thoroughly. If at the equivalence-point the formaldehyde concentration is 16%, the acid ionization constants have the following apparent values, expressed as their negative logarithms:

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[21] S. P. L. Sörensen, *Biochem. Z.*, **7**, 45 (1907); **25**, 1 (1910). V. Henriques and S. P. L. Sörensen, *Z. physiol. Chem.*, **64**, 120 (1910). See also E. Abderhalden, *Handbuch der Biochemischer Arbeitsmethoden*, Urban & Schwarzenberg, Berlin 1912.

[22] H. Schiff, *Ann.*, **325**, 348 (1902).

[23] L. J. Harris, *Proc. Roy. Soc. London*, **B95**, 500 (1923).

[24] L. J. Harris, *Proc. Roy. Soc. London*, **B104**, 412 (1929).

Amino Acid	p_{K_a} in 16% CH_2O	p_{K_a} in H_2O	$\frac{K_a\,(CH_2O)}{K_a\,(H_2O)}$
Glycine	5.4	9.75	2.2×10^4
Alanine	6.4	9.7	2.0×10^3
Phenylalanine	5.9	9.1	1.6×10^3
Tyrosine	6.2	8.7	3.2×10^2
p_{K_2}	>9	9.7	
Aspartic acid	$\leqq 3.8$	3.8	
p_{K_2}	6.85	9.85	1×10^3
Glutamic acid	$\leqq 4.2$	4.2	
p_{K_2}	6.8	9.8	1×10^3

From the mass action principle it is to be expected that the apparent acid ionization constant should depend upon the formaldehyde concentration. Harris confirmed this in the case of glycine. The following values are estimated from graphs given in his paper:

CH_2O, %..............	0	0.5	2	8	16	32
p_{K_a}	9.75	7.8	6.8	5.7	5.4	4.8

At this point there should be noted an interesting fact which is commonly ignored in physiological chemistry. The effect of alcohol on amino acids is not directly comparable with that of formaldehyde. Alcohol lowers the ionization constants of both the basic and acidic groups, while formaldehyde, which is used in smaller concentrations, strongly lowers only the constants of the basic groups. Harris, for example, showed that the neutralization curve of an amino acid with a strong acid is unaffected by the presence of formaldehyde.

Sörensen recommended that in the titration of amino acids with alkali a large excess of neutral formaldehyde should be added, to shift the equilibrium as far as possible in the desired direction.

Procedure: To a neutralized sample corresponding to about 25 ml. of 0.1 N amino acid add 5 ml. of 37% formaldehyde, previously neutralized to phenolphthalein, and titrate with 0.1 N alkali until the color with this indicator appears distinctly rose-red (p_T about 9.0).

Northrop[25] recommended a variation of the procedure. The solution is so diluted that 5 ml. will require about 5 ml. of 0.01 N alkali in the final titration. Approximate preliminary neutralization is made to neutral red with strong alkali, to keep the volume small, and is completed with 0.01 N sodium hydroxide. Then 1 ml. of formaldehyde and a drop of phenolphthalein are added and titration with 0.01 N alkali is continued to the end-point.

[25] J. H. Northrop, *J. Gen. Physiol.*, **9**, 767 (1926); *Chem. Abstracts*, **20**, 3476 (1926).

In the titration of amino acids or simple polypeptides the results agree with those obtained electrometrically, yet not all amino acids can be determined exactly in this way. Glycine and other simple amino acids respond satisfactorily; if the compounds have stronger basic groups, the end-point occurs too soon. Thus in the formol titration of lysine Harris found that of the theoretical quantity of alkali only 86% was required at the normal end point (p_T = 8.8), 93% at 9.1, and 97% at 9.5. The true basic ionization constant of lysine is about 10^{-2}; upon addition of aldehyde it is diminished but still remains larger than that of glycine. In this case it is better to neutralize first to phenolphthalein in 85% alcohol and then proceed with the formaldehyde addition, etc. From the foregoing, one can also see that the use of thymolphthalein is advantageous in cases where the phenolphthalein end-point comes too soon.

Though a complete theoretical treatment of the alcohol and formol titrations of amino acids cannot be given at the present time, a helpful beginning has been made by Harris.[24] These matters have especial interest in physiological work, since the titration values obtained there do not always point in the right direction.

The formal titration has an important application in the determination of albumin (as in milk). The procedure, which is purely empirical, is the same as that given on p. 160; the titration is generally considered to represent amino nitrogen but in many cases may include other forms. A thorough theoretical investigation would be desirable in this field.

Secondary amines also react with formaldehyde:[26]

$$2R_2NH + CH_2O \rightleftarrows R_2NCH_2NR_2 + H_2O$$

The product is actually a stronger base than the original secondary amine. From this it is clear that formol titrations of proline and histidine, both of which contain imino groups, lead to erroneous results.

Salts of Alkaloids and of Aliphatic Amines, in the Presence of Alcohol: According to Foreman,[27] primary, secondary, and tertiary amines, and basic methylene derivatives of secondary amines, do not react alkaline to phenolphthalein in 80% alcohol. On this fact is based a titration of the acid component of their salts.

An important practical application is made in titrating salts of alkaloids. In water most alkaloids have ionization constants of about 10^{-6}, the constants being diminished by addition of alcohol. Such alkaloids no longer react alkaline to phenolphthalein in 50% alcohol. If care is taken that at the end-point the alcohol content does not fall below 40 to 60%, it is possible to titrate to phenolphthalein the acid combined with the following alkaloids: aconitine, apomorphine, cocaine, codeine, coniine, dionine, narcotine, papaverine, pilocarpine, quinine and the other cinchona alkaloids, and thebaine.

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[26] S. L. Jodidi, *J. Am. Chem. Soc.*, **40**, 1031 (1918).

[27] F. W. Foreman, *Biochem. J.*, **14**, 451 (1920).

Salts of brucine, morphine, and strychnine may be determined without alcohol, using phenolphthalein. On the contrary, atropine, emetine, and novocaine base are so strong that they react alkaline to this indicator even in 50% alcohol. In order to titrate their salts it is appropriate to add 5 or 10 ml. of chloroform to the water solution and neutralize to phenolphthalein until the rose color remains after shaking. The free alkaloid is almost quantitatively extracted and so does not interfere in the aqueous phase.

Acidimetric Determination of Amino Nitrogen: Linderström-Lang[28] developed a method for the titration of amino nitrogen in amino acids, dipeptides, amides, etc., with alcoholic hydrochloric acid (0.1 N HCl in 90% alcohol) using α-naphthyl red[29] as indicator.

The indicator solution is prepared by dissolving 0.1 g. of α-naphthyl red (benzeneazo-α-naphthylamine) in 100 ml. of 96% alcohol. In water the transition interval is from 3.7 (red) to 5.0 (yellow).

Procedure: To 10 ml. of the aqueous solution add 10 drops of indicator and titrate with alcoholic hydrochloric acid until the liquid is distinctly red. Then introduce enough acetone so that the solution will just remain clear and continue titrating until the color is slightly more red than the reference standard (see below). Add more acetone, to make its total volume 100–200 ml., and complete the titration to the color of the reference solution. The end-point is perceptible within 0.02–0.04 ml. of 0.1 N acid.

Linderström-Lang recommended two comparison solutions: **I** consists of 10 ml. water, 10 drops of indicator, 100–200 ml. of acetone, and 0.53 ml. of 0.1 N hydrochloric acid (the color corresponds to that of α-naphthyl red in water at a p_H of 5.1). **II** is similar to **I** but contains 1.10 ml. of 0.1 *N* hydrochloric acid (water color at p_H 4.8). In general it is advisable to use 200 ml. of acetone and titrate to the color of solution **II**.

Notes: (1) Since most amino acids and peptides are insoluble in acetone, the titration should be started in water solution and the acetone added later, after which the titration is completed quickly. In most cases the final solution is clear, but lysine dichloride and histidine chloride crystallize out rapidly. In such cases 200 ml. of acetone must be used.

(2) According to Linderström-Lang the method determines all of the nitro-

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[28] K. Linderström-Lang, *Z. physiol. Chem.*, **173**, 32 (1928).

[29] S. P. L. Sörensen, *Compt. rend. trav. lab. Carlsberg*, **8** (1909).

gen in monoamino carboxylic acids, diamino monocarboxylic acids, aminohydroxy monocarboxylic acids, proline, and hydroxyproline. It includes 50% of the nitrogen in asparagine, arginine, tryptophane, and dipeptides, 66.6% in histidine, and 33.3% in creatine and guanidine.

The basic group in taurine is too weak to be titrated. Urea binds a little acid but cannot be determined in this way; the same is true of potassium nitrate.

(3) Bases bound to weak or moderately strong acids can also be titrated in the manner described. Linderström-Lang was able to determine acetates, citrates (to citric acid), and phosphates (to phosphoric acid) quite accurately (cf. p. 153). In a later investigation[30] he made use of 2,4,2′,4′,2″-pentamethoxytriphenylcarbinol in place of α-naphthyl red.

(4) Richardson[31] thoroughly investigated titrations in 90% acetone (p. 153) and called attention to the fact that actually carboxyl groups are determined in amino acids, rather than amino groups:

$$RCOO^- + H^+ \rightarrow RCOOH$$

(5) In glacial acetic acid amino acids behave as strong bases[32] and according to Nadeau and Branchen[33] they can be titrated with a solution of perchloric acid in the same solvent. Crystal violet, α-naphtholbenzein, and benzoyl auramine are useful as indicators. Accurate titrations of glycine, *dl*-α-amino-*n*-valeric acid, *dl*-β-phenylalanine, *l*-tyrosine, *l*-cystine, *d*-glutamic acid, *l*-aspartic acid, *d*-arginine, *d*-lysine, *l*-proline, and *l*-tryptophan are possible.

4. Determination of Sulfate after Precipitation as Benzidine Sulfate.—Benzidine is a weak base which forms slightly soluble salts with various anions, such as sulfate, oxalate, and ferrocyanide. This property of benzidine makes possible a simple determination of these ions, that of sulfate having been studied the most thoroughly because of its practical importance. Benzidine has an ionization constant of about 10^{-9}; a dilute aqueous solution does not react alkaline to phenolphthalein. In the sulfate determination, benzidine sulfate is precipitated, filtered out and titrated warm with sodium hydroxide to phenolphthalein:

$$C_{12}H_8(NH_2)_2 \cdot H_2SO_4 + 2OH^- \rightarrow C_{12}H_8(NH_2)_2 + SO_4^= + 2H_2O$$

The accuracy of the method depends primarily upon the solubility of benzidine sulfate. The solubility rises with increasing acidity (formation of HSO_4^-) and generally also with increasing electrolyte content, but is diminished, as would be expected, in the presence of an excess of the precipitant. According to Bisson and Christie[34] the solubility in water at 25°C. amounts to 0.098 g. per liter. Meldrum and Newlin[35] found the following values for the solubility in hydrochloric acid solutions:

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[30] K. Linderström-Lang, *Z. physiol. Chem.*, **174**, 275 (1928).

[31] G. M. Richardson, *Proc. Roy. Soc. London*, **B115**, 121, 142, 170 (1934); a good theoretical discussion is given in these papers and also in one by A. Neuberger, *ibid.*, **B115**, 180 (1934).

[32] I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1014 (1934).

[33] G. F. Nadeau and L. E. Branchen, *J. Am. Chem. Soc.*, **57**, 1363 (1935). For the determination of dimethyl aniline, see H. Haslam and P. F. Hearn, *Analyst*, **69**, 141 (1944).

Hydrochloric Acid Concentration, *moles/liter*	Benzidine Sulfate Solubility, *g./1000 g. solution*	Hydrochloric Acid Concentration, *moles/liter*	Benzidine Sulfate Solubility, *g./1000 g. solution*
0.239	0.542	2.074	1.790
0.530	0.942	2.825	1.930
1.009	1.253	4.139	1.887

Vaubel,[36] who apparently originated the method, gave considerably lower figures for the solubility. Several authors[37] have studied and improved the method, while others[38] have applied it to determinations of sulfate in drinking water and in various solutions, such as those obtained after the oxidation of other forms of sulfur. The procedure given below[39] has been found to yield good results.

Reagent: Dissolve 6.7 g. of pure benzidine base in 20 ml. of 6 N hydrochloric acid and dilute with water to one liter (reagent of Friedheim and Nydegger).

Procedure: To 25 ml. of about 0.1 N sulfate solution, which should not be more than 0.5 N in free mineral acid, add 50 to 75 ml. of benzidine hydrochloride reagent while stirring. Allow to stand for 15–30 minutes, then filter with gentle suction on a paper protected from tearing by a perforated porcelain plate or platinum cone (a Lorenz crucible is suitable). Wash out the flask with some of the filtrate and rinse the precipitate five times with 3 ml. portions of water each time, sucking dry after each rinsing. Transfer the filter and precipitate to a flask or beaker (see Note 7), dissolve the benzidine sulfate by shaking with water at 50–75°C., and while still warm titrate with 0.1 N sodium hydroxide to a permanent red color of phenolphthalein. Toward the end the color fades several times, apparently because the precipitated benzidine occludes a little benzidine sulfate which then reacts slowly with excess alkali. The addition of some neutral alcohol to dissolve the free benzidine may be recommended. The titration of 0.05–0.1 N solutions may be made accurately within 0.5 or 1%.

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[34] C. S. Bisson and A. W. Christie, *Ind. Eng. Chem.*, **12**, 485 (1920).

[35] W. B. Meldrum and I. G. Newlin, *Ind. Eng. Chem., Anal. Ed.*, **1**, 231 (1929).

[36] W. Vaubel, *Z. anal. Chem.*, **35**, 163 (1896). See also Couturier, *Dissertation*, Tübingen 1897.

[37] W. Müller, *Ber.*, **35**, 1587 (1902); *Z. angew. Chem.*, **16**, 653 (1903). F. Raschig, *ibid.*, **16**, 617, 818 (1903); **19**, 331, 334 (1906); **40**, 864 (1927). W. Müller and K. Dürkes, *Z. anal. Chem.*, **42**, 477 (1903). C. Friedheim and O. Nydegger, *Z. angew. Chem.*, **20**, 9 (1907).

[38] H. Leffman, *Chem. Zentr.*, **1907, I**, 372. G. von Knorre, *ibid.*, **1910, I**, 1989; *Z. anal. Chem.*, **49**, 461 (1910). O. Nydegger, *Chem.-Ztg.*, **52**, 318 (1928). Vlastimil and M. Matula, *ibid.*, **50**, 486 (1926). F. Foerster and E. Haufe, *Z. anorg. allgem. Chem.*, **177**, 17, 21 (1928). E. L. Skau and I. L. Newell, *Ind. Eng. Chem., Anal. Ed.*, **5**, 180 (1933).

[39] I. M. Kolthoff, unpublished experiments.

Notes: (1) Müller[37] suggested precipitating the neutral sulfate solution hot with excess benzidine hydrochloride solution of known acid content and titrating an aliquot of the filtrate, but this procedure is not advisable.

(2) Errors are caused by coprecipitation of benzidine hydrochloride with the sulfate, giving high results, and by the solubility of benzidine sulfate, giving low results. By precipitating cold the error may amount to +0.5 to 1%, while by precipitating hot it is more likely to be about −0.5%.

(3) Good results were obtained in the presence of neutral salts such as potassium chloride, sodium chloride, or calcium chloride (up to 1 g. of $CaCl_2 \cdot 6H_2O$ in 25 ml. of 0.1 N sulfate). Nitrate in amounts of 2 g. of potassium nitrate per 25 ml. of 0.1 N sulfate led to positive errors of about 3% with cold precipitation, but better values were found using hot solutions. No deviations could be ascribed to the presence of 100 mg. of nickel, cobalt, aluminum, manganese, ferrous or ferric iron, chromium, zinc, or manganese.

(4) In agreement with Friedheim and Nydegger,[37] no disturbance due to ferric salts was encountered, though Raschig said the method could not be used in their presence. He made the iron harmless by reducing with hydroxylamine or hydrazine. It was shown by von Knorre[38] that Raschig had worked with impure (technical) benzidine which caused the difficulty. Much better results were obtained with the use of pure benzidine, which is to be advised in any case; nevertheless von Knorre recommended the reduction with hydroxylamine.

(5) Anions such as chromate, oxalate, ferrocyanide, and ferricyanide, which form slightly soluble salts with benzidine or which oxidize it, interfere in the sulfate determination. Various organic substances like starches and picrates also have a disturbing action.

✓(6) For the titration of 25 ml. of 0.01 N sulfate 10–20 ml. of precipitant is added and 3 or 4 hours are allowed before filtration. Because of the solubility, the results come out 3–4% low; they are not improved by longer standing or by a greater excess of reagent. In determining sulfate in 100 ml. of 0.002 N solution with 50 ml. of reagent, the error is about 6%, and it increases with further dilution. These weak solutions are best precipitated hot since the filtration is then easier and the precipitate dissolves better during neutralization. It is advisable to titrate at the boiling point with phenol red as indicator.

(7) Since the benzidine sulfate is difficult to remove quantitatively from the precipitation vessel, the titration is preferably carried out in the same vessel.

5. Titration of Sulfides and Bisulfides.—The displacement titration of an alkali sulfide to bisulfide involves the same difficulties as the titration of carbonate to bicarbonate. Because the ionization constants of hydrogen sulfide are smaller ($K_1 = 5.7 \times 10^{-8}$, $K_2 = 1.2 \times 10^{-15}$), the solution is more alkaline at the equivalence-point and the probable error is considerably greater. Theoretically a p_T of about 11 should be attained. Approximate results are possible if one titrates with hydrochloric acid to the color change of thymolphthalein from a strong blue to a medium blue. Carbonate should first be removed with barium or strontium chloride (see below).

Titration to the point at which all hydrogen sulfide has been liberated is much more accurate. Methyl orange or bromophenol blue can be used as indicator, or an excess of acid may be added, the hydrogen sulfide expelled by boiling and the acid titrated back to methyl red or phenolphthalein. Alkaline sulfide solutions are not stable since they are easily oxidized with formation of polysulfides; on this account some free sulfur may appear during neutralization.

Jensen and Rasmussen[40] recommend a method for the analysis of sulfide-bisulfide mixtures which, though in general having no advantage over the titrations to thymolphthalein and methyl orange, may be useful in case the solution contains other substances that consume acid between these two end-points. The authors have had no experience with this method. Sulfide is first titrated to bisulfide with thymolphthalein as indicator, then formaldehyde is added and all of the bisulfide is titrated:

$$Na_2S + HCl \rightarrow NaHS + NaCl \qquad (a)$$

$$NaHS + CH_2O + HCl \rightarrow HSCH_2OH + NaCl \qquad (b)$$

With pure sulfide, (*a*) is equal to (*b*). If (*a*) exceeds (*b*) the difference represents free alkali, while if (*b*) is greater than (*a*) the difference is a measure of the original bisulfide.

Procedure: About 10 g. of the fused sulfide or 20 g. of crystallized material is dissolved in water, treated with 10 ml. of 10% barium chloride or strontium chloride solution and diluted to 1000 ml. After the precipitate has settled, a 25 ml. portion of the clear liquid is pipetted out, treated with 5 drops of 1% thymolphthalein solution and titrated with 0.1 N hydrochloric acid to a faint blue (*a* ml.). 10 ml. of 37% formaldehyde previously neutralized to phenolphthalein is added and the titration is continued to a light pink. At this point one waits several minutes, then completes the titration to colorless (*b* ml.).

Note: In analyzing a sulfide sample which does not contain thiosulfate, it would generally be better to determine the total sulfide iodometrically and to titrate the total alkalinity with hydrochloric acid as previously described, rather than to depend upon the thymolphthalein titration. Another possibility consists in treating the sulfide-bisulfide mixture with silver nitrate, whereby the bisulfide yields an equivalent amount of hydrogen ions that can be titrated after removal of the silver sulfide by filtration. Samples containing free sodium hydroxide might first be treated with an excess of standard nitric acid which could be titrated back after the silver precipitation and filtration. In this case carbonate would be included as hydroxide.

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[40] K. A. Jensen and O. V. Rasmussen, *Z. anal. Chem.*, **94**, 180 (1933). See also E. Podreschetnikoff, *Z. Farben-Ind.*, **6**, 388 (1907).

6. **Titration of Salts of Inorganic Bases.**—***Potassium:*** Solutions of potassium salts yield a red crystalline precipitate[41] with the sodium or magnesium salt of hexanitrodiphenylamine (dipicrylamine). The potassium salt dissolves in acetone and upon addition of excess standard acid the free dipicrylamine is liberated. This is very slightly soluble in water so that after removing the acetone, cooling and filtering, one can titrate the excess of mineral acid. Though it is generally preferable to determine the potassium gravimetrically,[42] the acidimetric procedure of Kolthoff and Bendix may be advantageous for routine analysis.

Reagents: Magnesium dipicrylaminate, 3% (0.065 N). Mix 12 g. of dipicrylamine with 5 g. of magnesium oxide and place in an Erlenmeyer flask with 400 ml. of water. Stir well, allow to stand 15 to 20 hours and filter.

Wash solutions. (*1*) Distilled water cooled in an ice bath. (*2*) Saturated solution of potassium dipicrylaminate in water, prepared by adding an excess of the potassium salt to water at room temperature and allowing to stand for several hours in an ice bath, then filtering or pipetting off the clear solution and keeping it in an ice bath.

Procedure: Place the sample in a 30 ml. porcelain crucible containing a glass stirring rod and an Emich porcelain filter stick, and adjust the volume so that the concentration is about 2 mg. of potassium per ml. Neutralize the solution with standard sodium hydroxide or hydrochloric acid using thymol blue as indicator. With constant stirring add dropwise a 50–100% excess of the magnesium reagent (7 ml. of reagent are needed for 10 mg. of potassium). Cool the crucible and contents for at least 15 minutes in ice water and then place in a shallow dish filled with ice water. With the filter stick mounted just above the bottom of the crucible, remove the supernatant liquid and suck the precipitate as dry as possible. Wash with 1 ml. of wash solution (*1*), then with three or four 1 ml. portions of (*2*), and finally again with 0.5 ml. of (*1*). Replace the receiving vessel by a clean one and with the filter stick connected allow acetone to run drop by drop down the sides of the crucible and be drawn into the receptacle. After all the precipitate has been dissolved and the acetone comes over colorless, disconnect the receptacle and dilute the acetone solution with 5 to 10 ml. of water, warming to ensure complete solution of the potassium salt.

Add a measured excess of standard acid and place the vessel on a steam bath to coagulate the precipitated dipicrylamine and to remove the acetone. When no odor of acetone is noticeable, cool the mixture in ice water and filter off the amine on a sintered glass crucible, washing with ice water. Boil the combined filtrate and washings to expel carbon dioxide, and while still hot titrate with standard sodium hydroxide using bromothymol blue as indicator. Each milliliter of 0.1 N acid consumed corresponds to 3.91 mg. of potassium. The accuracy is within ±0.5% on samples containing 10 mg.

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[41] N. S. Poluektoff, *Mikrochemie*, **14**, 265 (1933–34).

[42] I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94

Notes: (1) Up to 100 mg. of sodium may be present with 10 mg. of potassium, but with larger amounts double precipitation is necessary.[42] Relatively large quantities of lithium, magnesium, and calcium do not interfere, but barium has to be removed.

(2) Metals which form precipitates in alkaline medium (iron, aluminum, etc.) may be removed by precipitation with a suspension of magnesium oxide.

(3) When phosphate or other anions capable of precipitating magnesium are present, a 3% sodium dipicrylaminate solution should be used in place of the magnesium reagent.

Ammonium Salts (see also pp. 155, 158): Ammonia is liberated from its salts by strong bases such as sodium hydroxide or potassium hydroxide; it may be determined quantitatively by distillation into an excess of standard acid which is then titrated back in the presence of methyl red or methyl orange. Various types of distillation apparatus are available (Figs. 12 to 14).

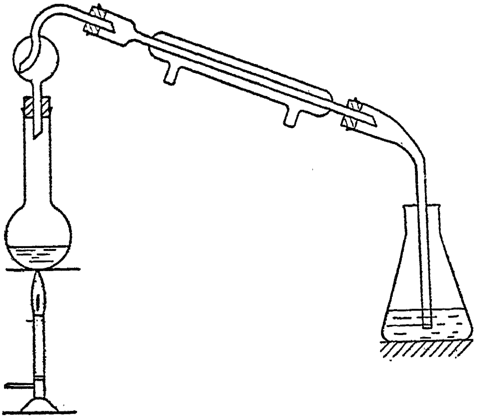

FIG. 12. Ammonia Distillation Apparatus (according to Biltz).[43]

In general a measured quantity of acid is first placed in the receiver, the sample is placed in the distilling flask and finally an excess of strong alkali is quickly introduced, with precautions against the loss of ammonia vapors. After the flask has been stoppered and the contents mixed well, heat is applied. Steaming out of the ammonia is greatly facilitated by bubbling through the reaction mixture a stream of ammonia-free air, nitrogen, or hydrogen from a fine orifice. This also makes for smooth boiling and diminishes bumping of the alkali; otherwise boiling stones (pumice, ceramic chips, or silicon carbide) should be placed in the flask. A trap or at least a bulb of glass wool above the distillation flask, before the bend of the ascension tube, is advisable to prevent entrainment of alkali.

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[43] H. Biltz and W. Biltz, *Ansführung quantitativer Analysen*, Hirzel, Leipzig, 1930, p. 184.

The vapor can be cooled either in a Liebig condenser connected with the receiver by means of an adapter, or in the receiver itself by placing the latter in a reservoir of water. Kretzschmar[44] uses as receiver a Pelligot U-tube, on the middle bulb of which is a short glass tube. This is closed with rubber tubing and a pinch clamp during distillation and is opened for easy washing out of the solution before back-titration. Distillation is considered to be complete when the liquid in the flask drops to one-half or one-third of its original volume. It is well, however, to test an additional drop of the distillate for ammonia with litmus paper.[45]

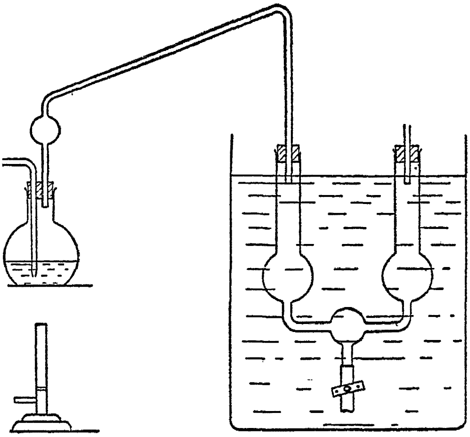

FIG. 13. Ammonia Distillation Apparatus (according to Kretzschmar).[44]

Winkler[46] suggested collecting the ammonia in 2% boric acid solution and titrating it directly with standard acid, thus avoiding the use of standard alkali. Methyl orange, which is used as indicator, is scarcely affected by boric acid (*cf.* p. 116). Wagner[47] places 4% boric acid in the receiver and titrates the ammonia to methyl red indicator, using a comparison solution. For smaller quantities of ammonia Ma and Zuazaga[48] recommend the Winkler method with 2% boric acid, titrating with 0.01 N hydrochloric acid and employing a mixed indicator composed of one part methyl red and five parts bromocresol green.

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[44] W. Kretzschmar, *Dissertation,* Dresden, 1932; *Z. anorg. allgem. Chem.,* **219,** 26 (1934).

[45] A worthwhile theoretical discussion of the best conditions for ammonia distillation, based on Henry's law, is given by H. Egner and V. J. Johannson, *Ann. Agr. Coll. Sweden,* **5,** 113 (1938).

[46] L. W. Winkler, *Z. angew. Chem.,* **26,** 231 (1913).

The use of a closed distillation system, provided with a rubber safety balloon to relieve the pressure, is recommended by Bradley.[49] This device prevents volatilization of ammonia from the receiver and renders unnecessary the use of excess standard acid or even boric acid. Bradley obtained results at least as accurate as those to be expected by the classical procedure.

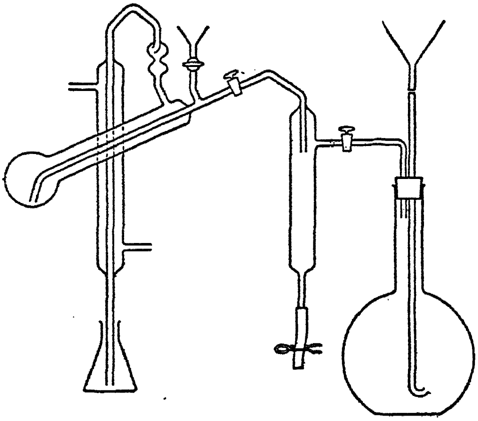

Fig. 14. Microdistillation Apparatus (according to Shrader).[51]

An apparatus for rapid microdistillation of ammonia was designed by Parnas and Wagner.[50] The form shown in Figure 14 has been found very convenient[51]; it can also be used for quick routine analyses of semimicro or even macro quantities and for other purposes, such as for the evolution of ammonia from those nitriles which are hydrolyzed by strong alkali, and, under the proper conditions, for distillations of iodine, phenol, and other substances that are volatile with steam.

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[47] E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **12**, 771 (1940).

[48] T. S. Ma and G. Zuazaga, *Ind. Eng. Chem., Anal. Ed.*, **14**, 280 (1942). J. F. Reith and W. M. Klazinga, *Chem. Weekblad*, **38**, 122 (1941), employed a mixture of slightly different proportions.

[49] J. A. Bradley, *Ind. Eng. Chem., Anal. Ed.*, **14**, 705 (1942).

[50] J. K. Parnas and R. Wagner, *Biochem. Z.*, **125**, 253 (1921).

[51] S. A. Shrader, unpublished experiments. See also G. Kemmerer and L. T. Hallett, *Ind. Eng. Chem.*, **19**, 1295 (1927); P. L. Kirk, *Ind. Eng. Chem., Anal. Ed.*, **8**, 223 (1936); J. H. Brant and D. C. Sievers, *ibid.*, **13**, 133 (1941); and J. L. Hoskins, *Analyst*, **69**, 271 (1944).

For the micro ammonia determination one generally works with an excess of standard acid in the receiver. The excess may be determined either iodometrically or through back-titration with 0.01 N alkali to methyl red. The sample and strong alkali are washed into the flask through the lower funnel, with care to keep the total volume small, then the ammonia is steamed out into the receiver. After removal of the latter, the residue in the distillation flask is drawn back into the steam trap by momentarily shutting off the steam; several portions of rinse water are drawn back in the same way and after drainage of the steam trap the apparatus is ready for use again. The ammonia distillation and washing can thus be completed within 10 minutes.

Prater, Cowles, and Straka[52] recommend the diffusion method of Conway[53] for the determination of from 0.2–10 mg. quantities of ammonia. The diffusion unit consists of a Petri dish (either the top or the bottom) with rim ground to a plane surface and coated with vaseline so that the dish may be closed tightly with a circular glass cover plate. A 100 mm. dish is used with a 10 ml. sample. The cover is spotted with 13 drops of a viscous glycerol-boric acid solution (28 g. boric acid per 100 g. glycerol previously adjusted so that upon addition of the same quantity to the wash water a p_H of 5.0–5.1 is obtained). To the sample is added, without mixing, 5 ml. of a solution saturated with sodium metaborate and potassium chloride, and the cover is quickly put in position. Stronger alkali may be used in the dish if there is no danger of converting other forms of nitrogen into ammonia. The dish is rocked carefully to mix the contents and is allowed to stand for 3 hours for diffusion of ammonia from the solution into the boric acid spots. After absorption the cover plate is held vertically over a funnel in a 125 ml. flask and is washed thoroughly with water adjusted to a p_H of 5.0–5.1. The solution is titrated with 0.01 N hydrochloric acid using a mixed indicator of methyl red and bromocresol green (see p. 58).

When ammonia is to be determined in the presence of other nitrogen compounds which may decompose during ordinary distillation to form volatile bases, it is often possible to obtain good results with the aeration procedure of Folin.[54] Ammonia is driven out of the weakly alkaline solution at room temperature with a rapid stream of air;

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[52] A. N. Prater, E. J. Cowles, and R. P. Straka, *Ind. Eng. Chem., Anal. Ed.*, **14**, 703 (1942). See also R. C. Hawes and E. R. Skavinski, *ibid.*, **14**, 917 (1942).

[53] E. J. Conway, *Micro-diffusion Analysis and Volumetric Error*, Van Nostrand, New York 1940.

[54] O. Folin, *Z. physiol. Chem.*, **37**, 161 (1902).

under these conditions compounds such as urea, uric acid, or creatinine are not attacked. For the complete absorption of larger quantities of ammonia it is necessary to employ special apparatus, for example, the sintered glass gas bubbler proposed by Täufel and Wagner.[55] The porous plate forming the end of the delivery tube causes an extremely fine division of the air stream.

Liberation of ammonia from its salts by means of excess magnesium oxide has frequently been suggested in the literature. Täufel and Wagner obtained variable results, especially when an acid solution was first neutralized with magnesia. The magnesium salt so formed depresses the hydroxyl-ion concentration of the suspension so that not all the ammonia is liberated. Nevertheless the method has found considerable use in technical analysis.[56]

In the presence of nonvolatile organic bases, it is, according to Foreman,[57] advantageous to distill ammonia and volatile amines from about 87% alcohol. The volatility of bases is in general increased in this medium as compared to water, while the volatility of acids (other than carbonic) is diminished.

Nitrates: An important method of determining nitrates is based upon their reduction to ammonia, followed by distillation as described in the preceding paragraphs. The reduction may be brought about in alkaline solution by means of Devarda's alloy[58] (50% Cu, 45% Al, 5% Zn) or in nearly neutral solution with Arnd's alloy[59] (60% Cu, 40% Mg). The former is especially useful in qualitative analysis but has the the disadvantage for quantitative work that a fine mist of alkali entrained by the liberated hydrogen is only with some difficulty prevented from contaminating the distillate. In the Arnd procedure the alkalinity amounts only to what is produced in the reaction. Both methods find technical application, especially in the fertilizer industry.

Procedure with Devarda alloy: A sample containing the equivalent of about 0.4 g. of potassium nitrate is placed in the distillation flask and brought to a volume of 110 ml. with water. 5 ml. of alcohol and 40 ml. of 30% potassium hydroxide solution are added, then 2–2.5 g. of the finely powdered alloy. The apparatus is connected to the receiver containing 50 ml. of standard 0.1

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[55] K. Täufel and C. Wagner, *Z. angew. Chem.*, **41,** 285 (1928). *Cf.* P. H. Prausnitz, *Chem.-Ztg.*, **50,** 809 (1926).

[56] See, for example, *Official and Tentative Methods of Analysis.* 5th ed., Association of Official Agricultural Chemists, Washington, D. C., 1940, p. 27.

[57] F. W. Foreman, *Biochem. J.*, **22,** 208, 222 (1928).

[58] A. Devarda, *Chem.-Ztg.*, **16,** 1952 (1892); *Chem. Zentr.*, **1893,** I, 232. See also *J. Assoc. Official Agr. Chem.*, **8,** 410 (1924–1925).

[59] T. Arnd, *Z. angew. Chem.*, **30,** 169 (1917); **33,** 296 (1920).

N hydrochloric acid, and the mixture is warmed very gently to start the reaction. After half an hour, or when most of the hydrogen has been evolved, the heat is increased and about two-thirds of the solution is distilled over. The excess acid is titrated back with 0.1 N alkali to methyl red. A blank should be carried through the same procedure to compensate for any alkaline spray which passes through the trap.

Procedure with Arnd alloy: About 0.5 g. of saltpeter dissolved in 300 ml. of water is treated with 10 ml. of magnesium chloride solution (20% $MgCl_2 \cdot 6H_2O$) and 5 g. of the powdered alloy, then two-thirds of the solution is distilled over into 60–80 ml. of 0.1 N acid. The excess acid is titrated back against methyl red. Each milliliter of 0.1 N acid corresponds to 1.401 mg. of nitrogen.

Notes: (1) If ammonia is also present it may be determined by distilling one portion of the sample directly with alkali; the sum of the ammonia and nitrate nitrogen is then found after reduction of another portion.

(2) For certain purposes Ulsch[60] suggested reducing nitrate with iron in sulfuric acid solution, then adding alkali and distilling. Szebellédy and Schall[61] recommended the electrolytic reduction of nitrate with a copper or nickel cathode in a neutral solution containing boric acid. The ammonia ormed can be titrated directly with acid.

Nitrogen in Organic Compounds: Kjeldahl observed long ago[62] that the nitrogen of many organic compounds can be fixed as ammonium sulfate by digestion with sulfuric acid. Gunning[63] suggested the addition of potassium sulfate to raise the boiling point of the acid and thus accelerate the reaction. The use of 0.05 g. of cupric oxide or 1 g. of mercury as a catalyst was proposed by Arnold[64]; cupric sulfate or pure mercuric oxide can be used as well. Before the subsequent distillation of ammonia the copper or mercury should be precipitated with sulfide, since otherwise they form amino or ammino complexes and the distillation is not quantitative.

Procedure: Place a sample containing about 0.05 g. of nitrogen in a Kjeldahl flask and add 10 g. of powdered potassium sulfate (nitrogen-free), about 0.6 g. of mercury or mercuric oxide and 20 to 25 ml. of concentrated sulfuric acid. Warm gently as the organic material chars, then gradually increase the temperature until eventually the carbon is completely oxidized. During the early stages care must be taken to avoid too much frothing of the mixture. More sulfuric acid should be added if prolonged digestion is required, to replace that which boils away. Ordinarily the digestion takes at least two hours for materials such as wheat.

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[60] K. Ulsch, *Z. anal. Chem.*, **30**, 175 (1891).

[61] L. Szebellédy and B. M. Schall, *Z. anal. Chem.*, **86**, 127 (1931).

[62] J. Kjeldahl, *Z. anal. Chem.*, **22**, 366 (1883).

[63] J. W. Gunning, *Z. anal. Chem.*, **28**, 188 (1889).

[64] C. Arnold, *Chem. Zentr.*, **1886**, 337. C. Arnold and K. Wedemeyer, *Z. anal. Chem.*, **31**, 525 (1892).

Heat for 15 to 30 minutes after the acid has become entirely clear, then allow to cool and dilute cautiously with 200 ml. of water, cooling again. Transfer to a distillation flask or arrange for carrying out the distillation directly from the Kjeldahl flask. Introduce 25 ml. of a solution containing 40 g. of sodium sulfide per liter, meanwhile mixing well. Now, without mixing, carefully pour down the side of the flask about 50 ml. of strong sodium hydroxide solution (80 g. NaOH in 100 ml. of water) or enough to provide a definite excess. Connect immediately to the distillation apparatus and mix the two layers completely before applying heat. Distill the ammonia into boric acid or an excess of standard acid as previously described.

Note: Numerous attempts have been made to shorten the digestion time. Lauro[65] suggested the use of selenium or one of its compounds as a catalyst; other workers[66] maintain, however, that mercury alone is preferable to a selenium compound used either alone or in conjunction with mercury. Apparently the rapid clearing up of a mixture containing selenium does not necessarily indicate complete conversion of nitrogen into ammonia.

Stubblefield and DeTurk[67] report that quantitative results can be obtained by digesting for only 30 minutes if the digestion mixture consists of 25 ml. of sulfuric acid, 0.6 g. mercury, 10 g. dipotassium phosphate, and 6 g. ferric sulfate. The latter, which is insoluble in strong sulfuric acid, provides more surface for oxidizing action of the sulfur trioxide on organic matter. Bumping is eliminated by the presence of alkali phosphate.

The use of perchloric acid for oxidizing the organic matter has been proposed several times[68] but has met with disfavor because of a serious explosion hazard and some trouble with losses of nitrogen. These objections appear to have been overcome in the procedures of Pepkowitz and co-workers,[69] who first digest the sample for 10 minutes with sulfuric acid, sodium sulfate, and selenium oxychloride, then cool, introduce a small quantity of 35% perchloric acid (2 drops for microanalysis, 10 drops for macro), and warm very gently until clear.

The nitrogen of nitrates and some organic nitro compounds can be reduced to ammonia by a modified Kjeldahl digestion in which salicylic acid is added as a reducing agent.[70] The dry sample containing not more than 0.5 g. of alkali nitrate or its equivalent is treated with 35 ml. of a mixture containing 40 g. salicylic acid in one liter of sulfuric acid. After shaking and warming gently to start the reaction, allow the suspension to stand for an hour, then add 5 g. sodium thiosulfate and heat moderately for about 5 minutes until frothing stops. Add 10 g. potassium sulfate with 1 g. of mercuric oxide and complete the digestion as usual.

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[65] M. F. Lauro, *Ind. Eng. Chem., Anal. Ed.*, **3**, 401 (1931). See also H. C. Messman, *Cereal Chem.*, **9**, 357 (1932). R. A. Osborn and A. Krasnitz, *J. Assoc. Official Agr. Chem.*, **16**, 110 (1933); **17**, 339 (1934).

[66] S. R. Snider and D. A. Coleman, *Cereal Chem.*, **11**, 414 (1934). C. F. Davis and M. Wise, *ibid.*, **10**, 488 (1933). J. Jany and A. Morvay, *Z. anal. Chem.*, **114**, 120 (1938).

[67] F. M. Stubblefield and E. E. DeTurk, *Ind. Eng. Chem., Anal. Ed.*, **12**, 396 (1940). See also H. W. Gerritz and J. L. St. John, *ibid.*, **7**, 380 (1935); A. L. Prince, *J. Assoc. Official Agr. Chem.*, **26**, 54 (1943).

[68] See, for example, B. Mears and R. E. Hussey, *Ind. Eng. Chem.*, **13**, 1054 (1921).

[69] L. P. Pepkowitz, A. L. Prince, and F. E. Bear, *Ind. Eng. Chem., Anal. Ed.*, **14**, 856 (1942) (macro). L. P. Pepkowitz and J. W. Shive, *ibid.*, **14**, 914 (1942) (micro). See also A. L. Prince, *J. Assoc. Official Agr. Chem.*, **26**, 54 (1943).

The nitrogen of azo compounds, hydrazines, and certain nitro compounds is more difficult to convert completely into ammonia. Phelps and Daubt[71] give procedures suitable for various substances. Azo compounds are first refluxed with alcohol and either zinc dust or stannous chloride (or both) in hydrochloric acid; hydrazines are refluxed with alcohol, formaldehyde, zinc dust and hydrochloric acid for 15 minutes, then for an equal period after addition of 0.2 to 0.4 ml. of 40% stannous chloride in hydrochloric acid. In either case the mixture is finally diluted with water and evaporated to expel most of the hydrochloric acid before the sulfuric acid digestion is begun. Acetic acid may be employed as a solvent with advantage in some cases. The authors have reduced dinitrophenols by warming on a steam bath in the presence of 5 ml. glacial acetic acid and 1 g. zinc dust, then adding 1 ml. of 6 N sulfuric acid and allowing to stand over night at room temperature. Next morning the digestion is completed by the salicylic acid method previously described. Even after this prolonged process the result may be low by as much as 1% of the theoretical nitrogen.

Micro Kjeldahl digestions of amino compounds, etc.,[72] are performed on 10 mg. samples, each with 40 mg. mercuric oxide, 0.5 g. potassium sulfate, and 1.5 ml. sulfuric acid. The mixture is warmed until frothing stops and is then kept at boiling on a sand bath or digestion rack until it has been colorless for half an hour. After cooling, a drop of alcohol is added and the solution is again heated until colorless. An alternate method consists in digesting with sulfuric acid and using a little selenium as catalyst; after 15 to 20 minutes of boiling one may add 2 or 3 drops of perhydrol and heat again to clear the solution.[73]

For micro Kjeldahl decomposition of hydrazines, nitro, and nitroso compounds, Friedrich[74] refluxes the sample first with 1 ml. of strong hydriodic acid (sp. gr. 1.7) for 45 minutes, then distills off about 0.7 ml. of the acid, adds 0.5 g. potassium sulfate, 1 ml. water and 1.5 ml. sulfuric acid. The water and iodine are boiled out (with addition of another ml. of water and further heating if necessary), then 40 mg. of mercuric oxide is introduced and the usual Kjeldahl treatment is continued.

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[70] H. C. Moore, *Ind. Eng. Chem.*, **12**, 669 (1920). A. L. Prince, *J. Assoc. Official Agr. Chem.*, **8**, 410 (1925).

[71] I. K. Phelps and H. W. Daubt, *J. Assoc. Official Agr. Chem.*, **3**, 306 (1920).

[72] *Cf.* M. E. Lapp, *J. Assoc. Official Agr. Chem.*, **24**, 97 (1941).

[73] J. B. Niederl and V. Niederl, *Micromethods of Quantitative Organic Analysis*, Wiley, New York 1942, pp. 72–73. The use of hydrogen peroxide in Kjeldahl digestions was proposed by F. C. Koch and T. L. McMeekin, *J. Am. Chem. Soc.*, **46**, 2066 (1924).

[74] A. Friedrich, *Z. physiol. Chem.*, **216**, 68 (1933). A. Elek and H. Sobotka, *J. Am. Chem. Soc.*, **48**, 501 (1926), reduce these compounds by carrying out an ordinary digestion in the presence of 50 to 100 mg. of glucose. See also R. A. Harte, *Ind. Eng. Chem., Anal. Ed.*, **7**, 432 (1935), and M. E. Lapp, *J. Assoc. Official Agr. Chem.*, **24**, 97 (1941).

Urea: The hydrolysis of urea to ammonia and carbon dioxide is greatly accelerated by the enzyme urease at a p_H of close to 7. Marshall[75] based a method for the determination of urea on this hydrolysis. The enzyme is obtained from jack beans and is commercially available. Yee and Davis[76] determine urea and ammonia together after hydrolyzing the urea in a special aeration flask. A sample containing 50 mg. of urea is placed in the flask with 5 ml. of water and is neutralized if necessary; 0.1 g. of urease powder is added and the closed flask is placed in a bath at 40°C. for 15 minutes. After this period, the flask is connected with a bubbler in a vessel containing standard acid, and is partially evacuated. 20 ml. of alcoholic alkali (4 g. sodium hydroxide and 5 ml. of capryl alcohol in a liter of methanol) is added to the flask and the mixture is aerated for 15 minutes to drive over all the ammonia, the flask being kept in the 40° bath meanwhile. A duplicate sample is aerated without the urease hydrolysis for determination of the ammonia alone, the urea being determined by difference.

Note: More urease should be used in the presence of mercuric, cupric, or silver ions, which inactivate the enzyme. The activity may be partially restored by treatment with hydrogen sulfide.

Bismuth: The distillation method for ammonia was applied by Mahr[77] to the determination of bismuth. If to a bismuth salt solution one adds a strong solution of potassium bromide, the precipitate of basic bismuth bromide which first forms is redissolved and the mixture becomes faintly yellow. The complex bismuth bromide reacts quantitatively with $Co(NH_3)_6(NO_3)_3$ or $Cr(NH_3)_6(NO_3)_3$ to yield $Co(NH_3)_6BiBr_6$ or $Cr(NH_3)_6BiBr_6$. Mahr studied especially the latter; upon washing with water it hydrolyzes:

$$Cr(NH_3)_6BiBr_6 + H_2O \rightarrow \underset{\text{soluble}}{Cr(NH_3)_6Br_3} + \underset{\text{insoluble}}{BiOBr} + 2HBr$$

but it may be washed satisfactorily with 20% potassium bromide solution. The precipitate is then treated with alkali and the ammonia is determined after distillation.

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[75] E. K. Marshall, *J. Biol. Chem.*, **14,** 283 (1913); **15,** 487 (1914).

[76] J. Y. Yee and R. O. E. Davis, *Ind. Eng. Chem., Anal. Ed.*, **7,** 259 (1935). See also W. B. Griem and L. S. Walker, *J. Assoc. Official Agr. Chem.*, **24,** 867 (1941). E. J. Conway and E. O'Malley, *Biochem. J.*, **36,** 655 (1942), make use of a micro diffusion method.

[77] C. Mahr, *Z. anal. Chem.*, **93,** 433 (1933).

Procedure: Prepare the sample so that about 100 mg. of bismuth is present in about 75 ml. of moderately acid solution. Add 30% potassium bromide solution until the precipitated bismuth oxybromide redissolves, allowing several milliliters in excess, then neutralize the acid with sodium hydroxide solution added dropwise until the turbidity which forms at each drop will barely redissolve upon stirring. Filter a freshly prepared, saturated solution of $Cr(NH_3)_6(NO_3)_3$ in warm water and quickly add an excess to the bismuth solution at 40–50°C. The precipitate appears at once upon swirling the mixture. Allow to stand for 10–15 minutes with occasional shaking, cool under the tap or preferably with ice, filter on a glass crucible (G4), and wash with cold 20–25% potassium bromide solution. Since hexammino chromium salts are light-sensitive, the original salt, its solution, and the precipitate should all be protected from direct sunlight. The precipitate is washed completely into an Erlenmeyer flask with the aid of hot water, and the resulting mixture of $Cr(NH_3)_6Br_3$, potassium bromide, and suspended bismuth oxybromide is subjected to ammonia distillation after addition of alkali. Each milliliter of 0.1 N ammonia liberated corresponds to 3.483 mg. of bismuth.

Note: The procedure is quite specific for bismuth and is applicable in the presence of alkalies, alkaline earths, iron, manganese, chromium, nickel, cobalt, aluminum, zinc, and copper. If tin is present, 2 g. of tartaric acid should be added per 75 ml. of solution, with care taken (through suitable acidity) to prevent precipitation of potassium acid tartrate. In the presence of mercury, cadmium, or much zinc, tartaric acid is also added and the washed precipitate is transferred with hot water to a beaker, boiled for a few minutes to complete the hydrolysis, filtered on the same filter, and washed with hot water. The precipitate (bismuth oxybromide) is redissolved in warm 1 N hydrochloric acid containing 10% potassium bromide, and after addition of more 30% potassium bromide is reprecipitated as the chromium complex. Mahr expected to investigate further applications in the presence of lead, antimony, and silver.

Calcium Salts: Calcium hydroxide is a strong base and reacts strongly alkaline to phenolphthalein, yet the bound acid of its salts may be titrated using thymolphthalein if the solubility of calcium hydroxide is repressed by addition of much acetone. According to Willstätter and Waldschmidt-Leitz[78] one adds to the calcium salt solution an excess of alkali hydroxide and then enough acetone to make its concentration 85 to 90%. After 15 minutes the excess alkali is titrated back to permanent disappearance of the thymolphthalein color. The end-point is not sharp and the method is therefore not exact.

Magnesium Salts: Magnesium hydroxide also has strongly basic properties. Its salts consume no more alkali than do salts of the alkali metals, toward phenolphthalein. In the method of Willstätter and Waldschmidt-Leitz[78] one precipitates the salt solution with excess alkali and adds alcohol to a concentration of 66–75%. After 10 or 15 minutes the excess of alkali is titrated back toward thymolphthalein. In the presence of calcium salts methyl alcohol is used rather than ethyl.

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[78] R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **56**, 488 (1923). See also E. P. Schoch, *Ind. Eng. Chem.*, **19**, 112 (1927).

This method also lacks exactness. A better procedure[79] is based upon titrating the excess alkali in an aliquot part of the clear liquid after settling; no alcohol is necessary.

Procedure: To 25 ml. of about 0.1 N magnesium salt solution in a 100 ml. volumetric flask add at least 35 ml. of 0.1 N sodium hydroxide free from carbonate and dilute to the mark with water. After mixing, the suspension is allowed to settle and a 50 ml. portion of the supernatant liquid is pipetted out and titrated with 0.1 N hydrochloric acid, to phenolphthalein. The magnesium hydroxide settles rapidly enough so that ordinarily a sample may be taken within half an hour. The method is applicable in the presence of calcium salts if not too much alkali is added; in the absence of carbonate the error need not exceed 0.5%.

Notes: (1) A saturated solution of magnesium hydroxide in water reacts strongly alkaline to phenolphthalein. The solubility is about 2.5×10^{-4} molar, corresponding to a hydroxyl-ion concentration of 5×10^{-4} N or a p_H at 23°C. of about 10.7. In the presence of 0.01 N alkali the solubility is so strongly repressed that it can be neglected.

(2) From the foregoing it follows that a saturated magnesium hydroxide solution does not react alkaline to nitramine or tropeolin O. Therefore one might expect that a 1 N magnesium salt solution could be titrated directly with 1 N alkali and one of these indicators (see p. 155). Yet the determination cannot be recommended, because during precipitation basic salts are formed so that too little alkali is taken. Even under the best conditions the method is not accurate to within 1%.[79]

(3) The principle of the method described above is not new. Knöfler[80] applied it, precipitating hot and filtering after cooling. Other workers[81] have used the same idea, with the modification of adding alkali oxalate to render calcium harmless. In the authors' opinion it is better to pipette out the clear alkaline solution rather than to filter, because under these conditions less carbon dioxide is absorbed. Further, moderate amounts of calcium do not interfere at all, so this element need not be removed.

(4) The use of trinitrobenzene as indicator was suggested by Pierce, Setzer, and Peter.[82] It is very sensitive to hydrogen ions, showing its acid color in a suspension of magnesium hydroxide but being colored brick-red by an excess

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[79] I. M. Kolthoff, *Rec. trav. chim.*, **41**, 787 (1922).

[80] O. Knöfler, *Ann.*, **230**, 345 (1885).

[81] M. Monhaupt, *Chem.-Ztg.*, **27**, 501 (1903). L. Legler, *Pharm. Zentralhalle*, **45**, 585 (1904). A. Vürtheim, *Chem. Weekblad*, **19**, 461 (1922). E. Maigret, *Bull. soc. chim.*, **33**, 631 (1905).

[82] J. S. Pierce, W. C. Setzer, and A. M. Peter, *Ind. Eng. Chem.*, **20**, 436 (1928). J. S. Pierce and M. B. Geiger, *Ind. Eng. Chem., Anal. Ed.*, **2**, 193 (1930).

of alkali. The magnesium salt solution is titrated with sodium hydroxide to the red color, and a blank equal to the quantity of alkali required to produce the change in the same volume of water is deducted. Unfortunately the alkaline color of the indicator is not stable. Pierce and his co-workers applied the titration to the determination of magnesium in dolomite; the sample is dissolved in excess hydrochloric acid, boiled to expel carbon dioxide, and titrated back using bromothymol blue. (Methyl red should be more satisfactory, causing less color interference in the subsequent step.) The magnesium is then titrated as has been described. Errors of 1 to 2% may be encountered.

(5) The Willstätter and Waldschmidt-Leitz method has been improved by Rauch,[83] who applied it to the analysis of carnallite. The magnesium chloride mixture is treated with sufficient alcohol to make the concentration of the latter 70% by volume at the end-point, then excess alkali is added and back-titrated with acid to thymolphthalein. Too low values (0.4 to 1%) are found, apparently because some of the finely divided magnesium hydroxide reacts with acid.

Procedure: To the neutral magnesium solution are added five times its volume of 95% alcohol and a few drops of 0.1% thymolphthalein. The mixture is titrated with enough 0.5 N alkali to turn the liquid blue and provide an excess of 1 or 2 ml., then the flask is covered with a small funnel and heated on an asbestos gauze, meanwhile being swirled, until the liquid just boils. A rubber stopper is inserted to prevent carbon dioxide absorption and the mixture is allowed to cool for 10 or 15 minutes. More alcohol is added if necessary, along with 5 drops of indicator per 50 ml. of solution, and the excess alkali is titrated with standard hydrochloric acid. In case the alkali used contains carbonate, it will be titrated nearly to bicarbonate; standardization should be carried to the same point, but this does not eliminate the error entirely. Standardization against known amounts of magnesium would be better.

Small amounts of calcium (up to 20 mg.) are kept from interfering by the addition of 1 ml. of 1 N potassium oxalate. With larger quantities, some magnesium coprecipitates and low results are obtained. Whether or not interference occurs in the presence of much sulfate or other higher valence anions has not been tested.

Calcium and Magnesium; Hardness of Water: The determination of calcium and magnesium together according to the procedure of Wartha and Pfeifer[84] is of great practical importance in testing the hardness of water (see also the Blacher method, p. 192).

Procedure: The bicarbonate alkalinity of the water is first found by titrating 100 or 200 ml. with 0.1 N hydrochloric acid, to methyl yellow or methyl orange. The same liquid is then treated in a tall cylinder with at least twice the theoretical amount of a solution prepared by mixing equal volumes of 0.1 N sodium hydroxide and 0.1 N sodium carbonate (a mixture containing about 2.5 g. NaOH and 7.5 g. $Na_2CO_3 \cdot 10H_2O$ per liter). After standing overnight an aliquot part of the clear liquid is titrated back with hydrochloric acid, again to methyl yellow or methyl orange. A correction of 0.3 ml. of 0.1 N solution is applied per 100 ml. of the titrated solution, because of the solubility of calcium carbonate and magnesium hydroxide.

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[83] A. Rauch, *Z. anal. Chem.*, **84**, 336 (1931).

[84] J. Pfeifer, *Z. angew. Chem.*, **15**, 198 (1902).

Each milliliter of 0.1 N solution used per 100 ml. represents 2.8 German degrees of hardness (1 German degree = 10 mg. calcium oxide per liter).

Notes: (1) The Wartha-Pfeifer method has been covered extensively in the literature.[85] Originally Pfeifer neutralized the water against alizarin (methyl yellow is better), then added an excess of the carbonate and alkali, boiled for several minutes, cooled, diluted to 200 ml. at 15°C., and finally filtered. The above procedure of Winkler[86] is much simpler and gives very good results. The solubility correction was determined experimentally by the author.

(2) In titrating the alkalinity of the water to methyl yellow a correction of 0.1 ml. of 0.1 N acid per 100 ml. should be subtracted to allow for the titration error of the indicator. The end-point is taken at a deviation from the water tint. In determining hardness the correction need not be considered because the final titration is taken to the same end-point, and the solution is also standardized using the same indicator. In standardizing it is advisable to dilute with distilled water to a volume as great as that expected in the analysis.

(3) Cooper[87] correctly points out that the determination of bicarbonate hardness with methyl orange indicator leads to high results when the total carbonic acid content at the end-point (sum of the original bicarbonate and free carbonic acid) is lower than about 1.2 millimoles per liter (73 p.p.m. carbonic acid). He recommends the use of a mixed indicator composed of 0.02 g. methyl red and 0.1 g. bromocresol green dissolved in 100 ml. of 95% ethanol; three drops are added to 100–250 ml. of the solution. The mixture shows the following colors in solutions of given p_H values: blue with trace of green at 5.2 and above, light blue with lavender gray at 5.0, light pink gray with cast of blue at 4.8, light pink at 4.6, pink to rose below 4.6. Cooper takes the end-point at 4.85 with 30 to 50 p.p.m. of carbonic acid, 4.75 with 70 to 100 p.p.m., and 4.6 with 150 p.p.m. When 250 p.p.m. are present the titration is continued until the color becomes pink, then the solution is vigorously stirred for 30 seconds during which time carbon dioxide escapes and the color reverts to a pink with bluish cast. Enough acid is then added to restore the pink, this being taken as the final end-point.

(4) Iron interferes in the Wartha-Pfeifer method. According to Winkler[88] iron-bearing waters may be shaken with air and allowed to stand a few hours, then filtered through a pad of glass wool prior to the determination. All iron is precipitated as ferric hydrous oxide.

(5) If magnesium alone is to be determined, the water is first neutralized to methyl yellow and is boiled to expel carbon dioxide. Upon cooling it is neutralized to phenolphthalein and a known excess of carbonate-free alkali is

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[85] See especially H. Singer, *Chem.-Ztg.*, **42**, 289, 294, 307 (1918), where the literature is reviewed. Also E. von Cochenhausen, *Z. angew. Chem.*, **19**, 1987 (1906). E. Basch, *Chem.-Ztg.*, **28**, 31 (1904). M. Mayer and E. G. Kleiner, *J. Gasbeleucht.*, **50**, 321 (1907). O. Mayer, *Z. anal. Chem.*, **54**, 289 (1915). A. Heyn, *Oeffent. Gesundheitspflege*, **7**, 584 (1916); *J. Chem. Soc.*, **112**, **II**, 218 (1917). L. Grünhut, *Z. anal. Chem.*, **58**, 552 (1919). A. S. Behrman, *Philippine J. Sci.*, **11**, 291 (1916); *Chem. Abstracts*, **11**, 3354 (1917). G. Weissenberger, *Z. angew. Chem.*, **35**, 177 (1922). F. Kanhäuser, *Chem.-Ztg.*, **47**, 57 (1923).

[86] L. W. Winkler, *Z. angew. Chem.*, **34**, 115, 143 (1921). See also G. Bruhns, *ibid.*, **34**, 279 (1921).

[87] S. S. Cooper, *Ind. Eng. Chem., Anal. Ed.*, **13**, 466 (1941).

[88] L. W. Winkler, *Z. angew. Chem.*, **29**, 218 (1916).

Salts of Heavy Metals: In the titration of heavy metal salts with alkali there are commonly formed basic salts of variable composition. The equilibrium relationships are apparently complicated[89] and moreover equilibrium is usually not attained during a titration.

Lead Salts: Since a suspension of lead hydroxide reacts alkaline to phenolphthalein and also to thymolphthalein, one cannot titrate salts of lead directly with alkali. Vieböck and Brecher[90] found that lead easily forms a basic bromide which is neutral to phenolphthalein. At least a fivefold excess of bromide is necessary to prevent the taking up of too much alkali. The reaction is:

$$Pb^{++} + OH^- + Br^- \rightarrow PbOHBr$$

each ml. of 0.1 N sodium hydroxide corresponding to 20.72 mg. of lead (or the equivalent amount of bound acid).

Procedure: The solution of about two millimoles of lead salt in a volume of 50 ml. is heated to 50°C., treated with a gram or two of neutral potassium bromide and titrated with carbonate-free alkali to phenolphthalein, with continual shaking. Toward the end the mixture is heated again, somewhat more strongly.

Note: In case a basic salt such as basic lead acetate is present, the bound acid cannot be estimated directly but may be found in the following way. One portion is titrated as above, consuming a ml. of 0.1 N alkali. A duplicate portion is treated with 15–20 ml. of 0.1 N hydrochloric acid (accurately measured) and then with a solution of 1 g. of potassium sulfate in 15 ml. of water. After 2 minutes, back-titration is made with 0.1 N alkali to phenolphthalein and the volume of 0.1 N acid used up is recorded as b ml.

$$\text{Total lead in mg.} = 20.72\,(a + b)$$

$$\text{Lead oxide content as mg. Pb} = 20.72 \times 0.5b$$

$$\text{Lead acetate content as mg. Pb} = 20.72\,(a + 0.5b)$$

Zinc Salts: An aqueous suspension of zinc oxide is not alkaline to phenolphthalein. Ruoss[91] therefore adds to the zinc salt solution an excess of standard barium hydroxide, boils, and titrates back with hydrochloric acid. According to Howden,[92] zinc as the chloride can be titrated directly using phenolphthalein, while Hanak[93] found that zinc as the sulfate can also be determined if the titration is carried out at boiling. The author could not confirm this; even at boiling a basic salt is precipitated and the end-point with phenolphthalein comes too early. Addition of barium chloride improves the result but still does not make it exact. Direct titrations of zinc chloride or nitrate lead also to inexact results.

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[89] *Cf.* W. Feitknecht, *Helv. Chim. Acta*, **16**, 1302 (1933). E. Hayek, *Z. anorg. allgem. Chem.*, **207**, 41 (1931); **210**, 241 (1933); **216**, 315 (1934); *Monatsh.*, **65**, 233 (1935). The last paper deals especially with the titration of lead salts.

[90] F. Vieböck and C. Brecher, *Arch. Pharm.*, **270**, 109 (1932).

[91] Ruoss, *Z. anal. Chem.*, **35**, 143 (1896).

[92] R. Howden, *Chem. News*, **117**, 322 (1918).

[93] A. Hanak, *Chem.-Ztg.*, **43**, 691 (1919).

The purpose may be accomplished[94] by adding 25 ml. of the approximately 0.1 N zinc solution to 30 ml. of 0.1 N alkali, boiling for 3 minutes and then titrating back with acid to phenolphthalein. The end-point is not sharp and one must make the solution entirely colorless or too much alkali will be used, the zinc oxide apparently retaining this stubbornly. Results are not better than to 1%.

Cupric Salts: Ruoss[91] treats copper salts in the same way as zinc salts. The cupric oxide agglomerates quickly and the liquid is carefully titrated back with acid. The method at best is accurate only to 1% and cannot be well recommended.

Mercuric Chloride: The bound acid cannot be determined directly by titration with sodium hydroxide. A basic salt is formed and, moreover, the color of the precipitate interferes with recognition of the end-point. Rupp, Müller, and Maiss[95] found it best to reduce the precipitated mercuric oxide to mercury with hydrogen peroxide and then titrate the excess alkali:

$$HgCl_2 + 2NaOH \rightarrow HgO + 2NaCl + H_2O$$
$$HgO + H_2O_2 \rightarrow Hg + H_2O + O_2$$

Procedure: Add a measured amount of the mercuric chloride solution to a mixture of a known excess of 0.1 N sodium hydroxide with 10 ml. of neutral 3% hydrogen peroxide. Warm until the precipitate becomes entirely gray, cool, and add 30 ml. of water. Titrate the excess alkali to methyl red or methyl yellow.

The procedure gives good results. One may also titrate to phenolphthalein if the peroxide is first neutralized to this indicator. For 25 ml. of 0.05 M mercuric chloride the authors use 10 ml. of 3% peroxide solution and 30 to 35 ml. of 0.1 N sodium hydroxide. The mixture is heated with a soda-lime tube attached, the precipitate is allowed to settle for about 10 minutes, and, after cooling, the liquid is titrated back to phenolphthalein.

Bismuth Salts: Bismuth hydroxide is very slightly soluble, its saturated solution not reacting alkaline to phenolphthalein. The element has a strong tendency to form basic salts, however, so that direct titration with alkali leads to erroneous results. It is best to boil the bismuth salt solution with an excess of alkali and after cooling (soda–lime tube) to titrate back with acid to phenolphthalein. Accurate results can be obtained. According to the author's experience the precipitated bismuth hydrous oxide need not be removed as is recommended in many procedures.

Malaprade[96] determines bismuth in a different way. The slightly acid solution is neutralized with sodium hydroxide just to the yellow color of methyl red, after which 10 g. of sodium thiosulfate is dissolved in the solution and nitric acid is added until the indicator turns orange. At this stage the bismuth is present as a complex, $Na_3Bi(S_2O_3)_3$. A few drops of phenolphthalein are added and the solution is titrated with sodium hydroxide back through the yellow and to the first change to orange:

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[94] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **112**, 177 (1920).

[95] E. Rupp, K. Müller, and P. Maiss, *Pharm. Zentralhalle*, **67**, 529 (1926); *Chem. Abstracts*, **20**, 3537 (1926).

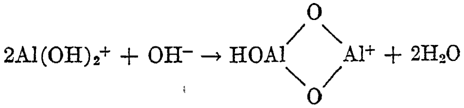
[96] L. Malaprade, *Ann. chim. anal. chim. appl.*, **22**, 5 (1940).

$$2Na_3Bi(S_2O_3)_3 + 5NaOH + NaNO_3 \rightarrow BiONO_3BiOOH + 6Na_2S_2O_3 + 2H_2O$$

The color change is not sharp, for the subnitrate compound reacts with more alkali to form the hydrous oxide. Malaprade obtained good results with bismuth solutions 0.05 M or stronger.

Aluminum Salts: Like most metallic salts, aluminum compounds upon precipitation with sodium hydroxide give basic salts. The composition of the precipitate depends especially upon the kind of anion present and upon the temperature. In the presence of multivalent anions the precipitate is much less basic than with univalent ions. Accordingly the end-points in titrations of aluminum sulfate or of alums with alkali are reached too early, because of sulfate coprecipitation. Long ago Erlenmeyer and Lewinstein[97] effected an improvement by adding barium chloride to remove the sulfate ions. Nevertheless the end-point with phenolphthalein still comes 2 to 2.5% too early. It is better to titrate to a pale rose at boiling. Upon cooling, the red color returns and one can titrate the small excess of alkali with a few drops of 0.1 N acid. Using aluminum chloride the theoretical result can be obtained[98] and the same is true of aluminum sulfate or of alum if an excess of barium salt is first added.

Treadwell and Zürcher[99] carried out a thorough investigation of the analysis of basic aluminum chloride solutions. Those having a molar ratio of Al : Cl = 1 are entirely clear and can undergo ultrafiltration without change. During potentiometric titration a significant break marks completion of the reaction:



$$2Al(OH)_2^+ + OH^- \rightarrow HOAl\begin{matrix}O\\ \diagup\quad\diagdown\\ \diagdown\quad\diagup\\ O\end{matrix}Al^+ + 2H_2O$$

this occurring at a p_H of 4.5–5.5. With further addition of alkali, hydrous aluminum oxide precipitates and the end-point is reached at a p_H of 8.5.

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[97] E. Erlenmeyer and G. Lewinstein, *J. prakt. Chem.*, **81**, 254 (1860).

[98] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **112**, 180 (1920). A. Tingle, *Ind. Eng. Chem.*, **13**, 420 (1921). See, however, H. L. Davis and E. C. Farnham, *J. Phys. Chem.*, **36**, 1057 (1932).

[99] W. D. Treadwell and M. Zürcher, *Helv. Chim. Acta*, **15**, 980 (1932).

In order to determine the basic salt content of a solution, Treadwell and Zürcher add an excess of acid to produce the normal salt and then back-titrate the excess potentiometrically or according to the oxalate method of Feigl and Krauss (see p. 111). They found the latter to give less accurate results.

Weiser, Milligan, and Purcell[100] failed to obtain a basic chloride in titrating dilute aluminum chloride solutions, apparently at room temperature. However, potentiometric titrations at 80°C. of aluminum chloride solutions containing ammonium chloride yield breaks which are stoichiometrically in agreement[101] with formation of the compound noted by Treadwell and Zürcher. The breaks are not sharp enough to be revealed closely with an indicator (0.1 ml. of 1 N alkali increases the p_H by about 0.2), but the potentiometric method has practical application for routine determinations of aluminum in magnesium alloys which may contain also manganese or zinc.[102]

If the aluminum salt solution contains free acid, this must first be neutralized. Methyl orange has been used as indicator[103] but the end-point is unsatisfactory.[104] It must be considered that aluminum salts show a strong acid reaction because of hydrolysis. The author determined the following p_H values colorimetrically using pure salts:

Molarity of Salt	p_H of Alum Solution	p_H of Aluminum Chloride Solution
0.1	3.4	
0.05	3.6	
0.02	3.9	3.55
0.01	4.05	3.7
0.005	4.15	3.8

Both the alum and aluminum chloride solutions therefore give transition tints with methyl yellow or methyl orange. In the titration of free acid a comparison solution of the correct p_H should be used. The end-point is still not sharp, however, because the p_H changes very gradually on addition of alkali. For this reason the method is of little importance. In practice, it would be better to determine the sum of aluminum and free acid on one portion of the sample and to determine the free acid separately on another portion by one of the procedures given on page 111, if the analysis could not be made potentiometrically.

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[100] H. B. Weiser, W. O. Milligan, and W. R. Purcell, *Ind. Eng. Chem.*, **33**, 669 (1941). See, however, H. W. Kohlschütter, P. Hantelmann, K. Diener, and H. Schilling, *Z. anorg allgem. Chem.*, **248**, 319 (1941); *Chem. Abstracts*, **36**, 4431 (1942).

[101] E. R. Wright and D. E. Lake, unpublished experiments.

[102] *Cf.* Scott's *Standard Methods of Chemical Analysis*, 5th ed., Vol. I, edited by N. H. Furman, Van Nostrand, New York, 1939, p. 540.

[103] C. R. Gyzander, *Chem. News*, **84**, 296, 306 (1901). Ruoss, *Z. anal. Chem.*, **35**, 150 (1896).

[104] G. Lunge and H. v. Kéler, *Z. angew. Chem.*, **7**, 669 (1894).

Other methods for determining aluminum by means of acid-base reactions are given by Germuth[105] and by Wöhlk,[106] both of whom first precipitate, filter, and wash the hydrous oxide. Germuth dissolves it in an excess of standard sulfuric acid and titrates back to methyl orange. Wöhlk uses an excess of oxalic acid with a little alkali oxalate and titrates back to methyl red (*cf.* p. 111). Neither procedure is capable of giving very exact results. Komárek[107] precipitates the hydrous oxide from alum solution with alkali at room temperature, the excess of base being removed by addition of hydrochloric acid until the pink color of phenolphthalein is discharged. The suspension of hydrous oxide is then titrated with standard hydrochloric acid until the solution becomes clear and bromophenol blue just turns yellow. Vieböck and Brecher[108] developed a procedure involving the formation of the barium salt of an aluminum tartrate complex. This is made just basic to phenolphthalein and is treated with potassium fluoride, whereby an amount of base equivalent to the aluminum is liberated and can be titrated.

Snyder[109] investigated the method of Vieböck and Brecher and proposed a slight modification, in which the preliminary neutralization is done with saturated barium hydroxide solution. The hydrochloric acid used for titrating is standardized against a known 0.3 N aluminum chloride solution, prepared by dissolving pure aluminum wire in a small excess of sodium hydroxide, barely acidifying with hydrochloric acid, boiling to expel carbon dioxide and making to an appropriate volume.

Procedure: Prepare the sample so that from 25 to 130 mg. of aluminum is present as chloride in an acid solution free from ammonium salts and interfering elements. Neutralize the free acid with barium hydroxide until a slight precipitate of aluminum hydroxide is formed, then add 30 ml. of 30% sodium potassium tartrate solution and complete the neutralization to a phenolphthalein end-point. Introduce 30 ml. of 30% potassium fluoride solution, previously neutralized to phenolphthalein. Titrate the liberated alkali with standard 0.3 N hydrochloric acid, to a point at which the solution becomes colorless and remains so for 30 seconds. Each milliliter of 0.3 N acid is equivalent to 2.7 mg. of aluminum.

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[105] F. G. Germuth, *Ind. Eng. Chem.*, **19**, 144 (1927).

[106] A. Wöhlk, *Dansk. Tids. Farm.*, **1**, 525 (1927); *Chem. Abstracts*, **22**, 3112 (1928). For the use of citrate in place of oxalate see A. C. Titus and M. C. Cannon, *Ind. Eng. Chem., Anal. Ed.*, **11**, 137 (1939); A. V. Pavlinova, *J. Applied Chem. U. S. S. R.*, **9**, 1682 (1936); C. H. Wood, *J. Soc. Chem. Ind.*, **63**, 317 (1944).

[107] K. Komárek, *Collection Czechoslov. Chem. Commun.*, **11**, 189 (1939).

[108] F. Vieböck and C. Brecher, *Arch. Pharm.*, **270**, 114 (1932); *Chem. Abstracts*, **26**, 3747 (1932).

[109] L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945).

Note: Interference is caused by manganese, magnesium, and trivalent chromium and iron if present in molar ratio to aluminum much greater than 0.01. Even smaller amounts of sulfate, and especially of silicate, cause high results, while phosphate causes low results. Calcium, copper, and zinc interfere if their molar ratio to aluminum is as great as 0.5.

If the hydrochloric acid used is standardized against an ordinary primary substance, the normality should be increased by 0.8% in order to give exact results in aluminum determinations.

Lanthanum Salts: Although lanthanum hydroxide is a strong base, its solubility is so low that the saturated solution does not react alkaline to thymolphthalein.[110] Yet the displacement titration of a lanthanum salt with sodium hydroxide fails to give useful values[111] because basic salts are formed and the indicator is hydrolytically adsorbed by the precipitate. Better results are obtained by reverse precipitation with an excess of sodium hydroxide or ammonia, followed by dissolution of the washed precipitate in acid and back-titration with alkali.

Procedure: The lanthanum salt solution is slowly added to 30–50 ml. of 1 N ammonia; after 10 to 20 hours the mixture is filtered and the precipitate washed with 50% alcohol in water, until the washings are no longer alkaline to phenol red. The precipitate is dissolved in an excess of standard hydrochloric acid, which may be titrated back with alkali to methyl orange, methyl red, or bromothymol blue. With the use of weight burettes, results accurate to 0.1% are possible. The method is of course subject to interference by other elements such as aluminum, iron, and the rare earths.

Beryllium Salts: Salts of beryllium can be titrated directly with alkali to phenolphthalein.[112] In the presence of fluoride there is some difficulty with formation of a complex salt. Zwenigorodskaja and Gaigerowa[113] destroy the complex (Na_2BeF_4) by adding to the solution, which contains no free acid, an excess of calcium chloride previously neutralized to phenolphthalein. They then titrate to this indicator, heating the mixture just to boiling at the end. The results are not very accurate but are useful for some practical purposes. Naturally many other elements interfere and must be removed.

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[110] According to I. M. Kolthoff and R. Elmquist, *J. Am. Chem. Soc.*, **53**, 1217 (1931), the p_H of a solution saturated at 25°C. is 9.1.

[111] I. M. Kolthoff and R. Elmquist, *J. Am. Chem. Soc.*, **53**, 1225 (1931).

[112] B. Bleyer and A. Moormann, *Z. anal. Chem.*, **51**, 360 (1912).

[113] V. M. Zwenigorodskaja and A. A. Gaigerowa, *Z. anal. Chem.*, **97**, 327 (1934).

Other Metals: Salts of most metals react with alkali to form basic compounds. If one wishes to convert such a salt into the oxide, it is generally necessary to add an excess of sodium hydroxide and back-titrate.

The studies of Britton,[114] concerning the p_H ranges in which various metal ions precipitate as hydroxides (or hydrous oxides), are very interesting from both the theoretical and practical standpoints. In analyzing mixtures one must always consider the probability that coprecipitation will occur, even though the p_H may be below that at which the contaminating element normally precipitates.[115]

A great deal of useful information concerning the hydrolytic precipitation of a number of elements has been accumulated by Gilchrist.[116] He generally worked with 100 mg. of an element, as a soluble salt in 150 to 250 ml. of boiling water, and carried out the precipitation with sodium hydroxide solution. His observations were made and reported in terms of the indicators which change at points of partial or complete precipitation, during gradual addition of sodium hydroxide or back-titration of an excess. The experiments were not designed with the purpose of extending volumetric methods (although helpful in that direction) but were intended to indicate possible procedures for separating various elements. Gilchrist has outlined several interesting separations in his paper.

In the following table are assembled data taken largely from Gilchrist but supplemented somewhat with values from Britton or from other sources available to the authors. In most cases the p_H values have been rounded off from the known indicator ranges; they should be regarded as mere approximations. Obviously the points of initial precipitation are governed by several factors, including the concentration of the element and of other electrolytes, the temperature, manner of introducing alkali, etc. It is assumed that ions such as phosphate, chromate, arsenate, and the like, which precipitate certain elements, are absent; however, carbonates have been present where noted in the table. Whether or not basic salts are formed has not been considered.

[114] H. T. S. Britton, *J. Chem. Soc.*, **127**, 2110, 2120, 2142, 2148 (1925); *Ann. Repts. Progress Chem.*, **40**, 45 (1943). See also J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 863 (1913). W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York 1929, p. 68.

[115] For data on the coprecipitation of divalent ions with ferric hydroxide precipitated by ammonia see I. M. Kolthoff and B. Moskovitz, *J. Phys. Chem.*, **41**, 629 (1937); I. M. Kolthoff and L. G. Overholser, *ibid.*, **43**, 767, 909 (1939).

[116] R. Gilchrist, *J. Research Natl. Bur. Standards*, **30**, 89 (1943).

HYDROLYTIC PRECIPITATION OF IONS

Ion	p_H of Probable Partial Precipitation	p_H Range of Complete Precipitation	Notes
Sn^{++++}	<1	1 to 6	Ppt. peptizes above 7, sol. in strong alkali.
Cb, Ta	<1	<1 to >10	
Ti^{+++}	1 or 2	(?)	Easily oxidized.
Ti^{++++}	1 or 2	6 to >10	
Zr, Hf	1 or 2	4 to >10	Points of initial pptn. have not been studied carefully.
Th	1 or 2	4 to >10	
Ce^{++++}	<2	3 to >10	
Hg^{++} (nitrate)	2		
Sn^{++}	3	(?)	Easily oxidized.
Hg$_2^{++}$	3		
Fe^{+++}	3	4 to >10	
Ga	<4	4 to 6	Completely sol. above 8.
In	<4	6 to 10	
UO$_2^{++}$	4	About 8	Incomplete pptn. in presence of carbonate.
Mn^{++++}	<5	About 8	
Pb^{++++}	<5	6 to >10	In presence of bromate.
Be	5	6 to 10	
Bi	5	7 to 8	Slightly sol. in absence of carbonate, or at p_H 10.
Al	5	6 to 7.5	Sol. in alkali.
Co^{+++}	6	8 to >10	In presence of bromate.
Ni^{+++}	6	8 to >10	In presence of bromate.
Zn	6	About 9	Sol. in alkali.
Cu^{++}	6	8 to >10	
Cr^{+++}	6	8 to 10	
Trivalent rare earths	6 or above	8 to 14	Depending upon element; those of lower at. wt. require a higher p_H.
Fe^{++}	7		Easily oxidized.
Pb^{++}	7	>8	In presence of carbonate; otherwise incomplete at any p_H.
Ni^{++}	7	8 to >10	
Ce^{+++}	7	8 to >10	Easily oxidized.
Cd	7	8(?)	Possibly complete in presence of carbonate.
Co^{++}	7–8	About 10	
Tl^{+++}	8		In presence of bromate.
Ag	8–9		Nitrites increase soly.
La	8–9	About 14	
Mn^{++}	8–9	9 to >10	Easily oxidized.

HYDROLYTIC PRECIPITATION OF IONS—*Concluded*

Ion	p_H of Probable Partial Precipitation	p_H Range of Complete Precipitation	Notes
Hg^{++} (chloride)	9(?)		
Mg	9–11	11 to >14	
Au^{+++}	>10		No ppt. up to p_H 10.
Tl^{+}	>10		
Ge^{++++}	>10		
Ca	12	14 and higher	Soly. decreases slightly at higher temperature.
Sr	14		Soly. increases greatly at higher temperatures.
Ba	14–15		

Gilchrist also studied the platinum metals, which have not been included in the table. Ruthenium, either tetravalent (as the chloro salt) or trivalent, is completely precipitated at 6.3; the former gives the best precipitate. Trivalent rhodium is precipitated completely in flocculent form upon complete neutralization. Divalent palladium is precipitated under the same conditions, though possibly not completely. In acidified bromate solutions, tetravalent rhodium and palladium are precipitated completely upon adjustment to between 6.3 and 8. The same is true of hexavalent iridium between 4 and 8. Tetravalent osmium is precipitated completely between 1.5 and 6.3, the best precipitate being obtained at 4. Tetravalent platinum as a chloro salt hydrolyzes very slowly at 6.3 but the precipitation eventually goes to completion. Apparently the hydrolysis is retarded by bromate.

Concerning the behavior of individual elements of the rare earth group, reference is made to the excellent work of Moeller and Kremers.[117]

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[117] T. Moeller and H. E. Kremers, *J. Phys. Chem.*, **48**, 395 (1944); *Chem. Revs.*, **37**, 97 (1945).

CHAPTER VI

TITRATIONS INVOLVING HYDROLYTIC PRECIPITATION OR COMPLEX FORMATION

1. Introduction; Sodium Carbonate as Reagent.—In these hydrolytic reactions one determines cations by precipitating them (or converting them into a complex) with the anions of the salt of a strong base and weak acid, or vice versa. So long as the ions being titrated are not quantitatively precipitated, the hydrogen-ion concentration changes but little as more reagent is added. At the equivalence-point, or when a slight excess of reagent comes into the solution, a greater change takes place. Thus the end-point can be located with a suitable indicator. Since the theoretical principles underlying these titrations have been discussed in Volume I (pp. 63–67), only the practical details will be considered here.

The ions of many metals may be precipitated as carbonates, yet their direct titration with sodium carbonate solution may not be satisfactory because the precipitate forms too slowly, as in the case of dilute solutions of alkaline earth salts, so that the end-point appears too soon. In other cases basic salt formation may cause a disturbance. Therefore special conditions have to be found for the titration of a particular metal.

Titration of Barium (and Sulfate): Barium chloride may be titrated with sodium carbonate solution to phenolphthalein if alcohol is added to repress the solubility of barium carbonate and to increase the speed with which it precipitates. Chalmers and Rigby[1] obtain the best results by titrating barium chloride in the presence of sufficient alcohol (90% ethanol, formula 30 denatured alcohol, or methanol) to make its concentration 35–60% at the end-point. In applying the titration to the rapid determination of sulfate, they slightly acidify 50 ml. or less of the sulfate solution with hydrochloric acid, boil to expel carbon dioxide and neutralize to phenolphthalein with 0.2 N sodium hydroxide. The solution should be filtered at this point if iron is present. Without cooling, 100 ml. of alcohol is added and then an excess of standard 0.1 N barium chloride solution is introduced from a pipette. The excess is titrated with 0.1 N sodium carbonate to a faint but permanent pink color of phenolphthalein.

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[1] A. Chalmers and G. W. Rigby, *Ind. Eng. Chem., Anal. Ed.*, **4**, 162 (1932). See also F. Litterscheid and K. Feist, *Arch. Pharm.*, **237**, 521 (1899). T. Cooksey, *J. Proc. Roy. Soc. N. S. Wales*, **41**, 216 (1907). C. Blacher and U. Koerber, *Chem.-Ztg.*, **29**, 722 (1905).

Note: The best conditions for precipitation of barium sulfate prior to back-titration of the excess barium have to be selected somewhat empirically. Chalmers and Rigby chose to carry out the precipitation from warm alcoholic solution. The authors have observed that if the barium chloride is added to sulfate in hot aqueous solution, too little sulfate is found (coprecipitation of sulfuric acid or alkali sulfate). Better results can be obtained by pipetting the sulfate solution into an excess of the hot aqueous barium chloride. In this case coprecipitation of barium chloride evidently brings about a compensation of errors.

It has also been noted that if the titration with sodium carbonate is performed rapidly too little of this reagent is used, apparently because some barium chloride is occluded by the barium carbonate precipitate. The authors have been led to the following procedure: Pipette duplicate 25 ml. portions of 0.1 M barium chloride solution into 400 ml. beakers and add to each 0.2 ml. of 4 N hydrochloric acid and a little silicon carbide to prevent bumping. Heat one just to boiling and pipette in 50 ml. of the sample, which has previously been made neutral or just slightly acid and has been brought to a definite volume such that the sulfate concentration is about 0.03 M. Cover the beaker, boil for 3 minutes, and cool under the tap. In the same way place in the second beaker 50 ml. of water (or of a blank solution containing any reagents previously employed in preparing the sample), boil, and cool. When ready to titrate, add 0.3 ml. of 1% phenolphthalein and 100 ml. of methanol to each beaker, bring just to the pink shade with 1 N sodium hydroxide, and then back just to colorless with 0.1 N hydrochloric acid. Titrate very slowly with 0.1 M sodium carbonate solution. The solution becomes pink with each addition, then fades as barium carbonate precipitates. The end-point is a change to a faint pink which does not fade after half a minute of vigorous stirring. Titrate the blank in the same way and just as carefully, since the calculation is based upon the difference between the two. About 10 minutes are required for each titration. One must avoid breathing into the beakers, since absorption of carbon dioxide causes fading of the pink color.

Titration of Zinc or Lead: According to Jellinek and Krebs[2] zinc and lead salts can be determined with sodium carbonate solution. To the dissolved zinc salt, neutralized using a little methyl orange as indicator, one adds an excess of 0.1 N sodium carbonate. The suspension is heated to boiling for about 5 minutes and titrated back with a standard neutral zinc sulfate solution until colorless to phenolphthalein, meanwhile being kept at boiling. Use of a comparison mixture, prepared by precipitation of the metal salt with soda but without addition of phenolphthalein, is recommended. The method has very little practical importance.

Komaretzkyj[3] titrates 0.1 to 0.025 N lead solutions directly with 0.1 N sodium carbonate, using phenolphthalein as indicator. The soda solution is allowed to drop in slowly while the mixture is stirred well, until a permanent pink color appears. This can be seen more readily if the precipitate is allowed to settle between additions of reagent near the end-point.

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[2] K. Jellinek and P. Krebs, *Z. anorg. allgem. Chem.*, **130,** 313 (1923). *Cf.* Ruoss, *Z. anal. Chem.*, **35,** 143 (1896).

[3] S. Komaretzkyj, *Z. anal. Chem.*, **84,** 407 (1931).

Note: Acid solutions are first neutralized to methyl orange and boiled to expel any carbon dioxide that may be present. Obviously the method fails if the solution contains non-volatile weak acids.

2. Potassium Palmitate as Reagent.—Like the other soaps of alkalies, potassium palmitate is strongly hydrolyzed in aqueous solution. It reacts with the salts of alkaline earths (and also of other metals) to form insoluble palmitates. If one adds an excess of potassium palmitate to a neutral alkaline earth salt solution, the mixture becomes definitely alkaline to phenolphthalein. The reagent was introduced by Blacher[4] for determining the hardness of water and is well suited for this purpose. The procedures recommended below for preparing the volumetric solution and carrying out the determination are essentially those of Winkler.[5]

Preparation of the Solution: In a 1.5 liter Erlenmeyer flask place 500 ml. of 95% ethanol, 300 ml. of distilled water, 0.1 g. phenolphthalein, and 25.6 g. purest palmitic acid.[6] Warm on a steam bath and add clear alcoholic potassium hydroxide, while rotating, until all the acid is dissolved and the solution becomes a faint pink. In case too much alkali is taken, it should be neutralized with a little hydrochloric acid and the solution brought back just to pink. (The potassium hydroxide solution is prepared by grinding 7 or 8 g. of the solid with 50 ml. of warm 95% alcohol). Allow the palmitate solution to cool and dilute to one liter with 95% alcohol.

Because palmitate may separate out in case a solution so prepared is cooled to 15°C., Winkler recommended making it to volume with propyl alcohol in place of ethyl; Blacher used neutral glycerin. If such a solution is filtered after several days, it will thenceforth remain clear even upon cooling to 0°.

Standardization: Blacher used lime water for standardizing palmitate solution. Winkler's procedure consists in preparing 40–50 ml. of clear lime water (from ignited marble and carbon dioxide-free distilled water) and titrating this with 0.1 N hydrochloric acid. One drop of 0.1% methyl orange is used as indicator. The neutral solution is diluted to about 100 ml. with ordinary distilled water and is treated with a drop of bromine water to decolorize the indicator. After addition of 0.5 ml. of 1% phenolphthalein, 0.1 N sodium hydroxide is introduced drop by drop until the solution becomes a distinct red which persists after standing for several minutes. The solution is then brought back just to colorless by dropwise addition of 0.1 N hydrochloric acid and shaking; one drop of the acid is added in excess.

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[4] C. Blacher, P. Grünberg, and M. Kissa, *Chem.-Ztg.*, **37**, 56 (1913).

[5] L. W. Winkler, *Z. anal. Chem.*, **53**, 409 (1914); *Z. angew. Chem.*, **34**, 143 (1921). See also G. Lunge and E. Berl, *Chemisch-technische Untersuchungsmethoden*, 7th ed., Springer, Berlin 1922, Vol. I, p. 483.

[6] According to K. Scheringa, *Chem. Weekblad*, **29**, 606 (1932), it is not necessary to employ pure palmitic acid, for the less expensive stearin (a mixture of palmitic and stearic acids) works as well. J. H. van der Meulen, *ibid.*, **38**, 429 (1941), uses a potassium stearate solution containing isobutyl or isopropyl alcohol. This is prepared by dissolving 28.4 g. of technical stearic acid in 200 ml. of isopropyl or isobutyl alcohol and adding 0.1 g. phenolphthalein and 100 ml. of 1 N potassium hydroxide free from carbonate. Enough more of the alkali is introduced to give a faint rose color, then 50 ml. of ethyl alcohol is added and the solution is diluted to a liter with water.

The mixture is now titrated with potassium palmitate solution while being shaken vigorously, until the snowy-white appearance caused by precipitation of calcium palmitate changes not merely to a perceptible pink, but to a pronounced red color which remains for several minutes. From the volume of palmitate consumed one deducts 0.3 ml. as a correction, or 0.2 ml. if the color was taken only to a faint pink. Assuming accurate preparation of the palmitate solution, the corrected volume should agree closely with the original 0.1 N hydrochloric acid titration.

Notes: (1) According to the authors' experience Winkler's procedure gives excellent results. The addition of a drop of acid in excess at the start is to be recommended, since otherwise the solution is pink throughout the titration and the deepening of the color at the end-point is less distinct.

(2) In place of lime water one may use a calcium chloride solution prepared from the pure crystalline salt and standardized argentometrically by Mohr's method. The solution may also be prepared from pure marble and an equivalent quantity of hydrochloric acid, with boiling to expel carbon dioxide.

(3) Phenolphthalein may be replaced as indicator by bromocresol purple (10 drops of 0.1% solution per 100 ml.). The end-point is then a deep purple-red color. The addition of 3 drops of 0.1 N acid in excess at the beginning is to be recommended in this case. Phenol red, neutral red, and bromothymol blue are not suitable indicators for the titration.

(4) The titer is independent of the amount of calcium that is titrated.

Procedure for Hardness Determination: Neutralize 100 ml. of the water to methyl yellow or methyl orange with 0.1 N hydrochloric acid (bicarbonate hardness). Expel carbonic acid by passing a stream of air through the liquid for several minutes, or by boiling and cooling. A small amount of carbon dioxide does not interfere; one can therefore blow out the carbon dioxide sufficiently well with small hand bellows as recommended by Blacher. Carry through the rest of the procedure just as in the standardization of palmitate solution.

Notes: (1) In agreement with Weissenberger[7] the senior author has found that a magnesium salt consumes a little more palmitate than does the equivalent quantity of a pure calcium salt. The difference in titer amounts to about 2%.

(2) The end-point is difficult to recognize if the sample is colored. Ordinarily the color can be destroyed by adding a milliliter of bromine water and boiling out the excess, after the preliminary neutralization. The liquid is then adjusted with alkali and acid as in the standardization.

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[7] G. Weissenberger, *Z. angew. Chem.*, **35**, 177 (1922).

(3) Iron, which interferes in the determination, is usually oxidized by aeration. This method is not entirely free from objection, however, since under some conditions calcium carbonate may also precipitate. Addition of bromine water can serve to oxidize ferrous iron, after which the boiled solution is treated with 10 ml. of 30% sodium potassium tartrate and neutralized, first to a pink with phenolphthalein and then back with a drop of 0.1 N acid in excess. Air oxidation of the iron in the presence of tartrate can also be employed. Tartrate prevents the precipitation of calcium carbonate by forming a soluble complex with calcium ions, but does not interfere in the palmitate titration.

Magnesium in the Presence of Calcium: Froboese[8] proposed a rapid method in which calcium interference is prevented by the addition of oxalate. The following procedure is somewhat modified from that which he suggested.

Procedure: To 200 ml. of the water sample add a slight excess of 0.1 N hydrochloric acid, enough so that the solution reacts definitely acid to methyl yellow. Heat to boiling and add 5 ml. of 10% potassium oxalate solution, drop by drop. After cooling, neutralize to phenolphthalein and then discharge the pink color with a drop of 0.1 N acid in excess. Titrate with palmitate solution to a permanent rose color and deduct a blank of 0.3 ml. from the titration.

Note: Satisfactory results can be obtained on samples of widely varying magnesium content. Since the magnesium titer of Blacher's reagent is about 2% lower than the calcium titer, standardization against pure magnesium sulfate is to be recommended.

Calcium in the Presence of Magnesium: Polsky and Feddern[9] determine calcium in industrial waters by means of Clark's soap solution,[10] eliminating the interference of small quantities of magnesium by titrating at p_H 11.7 (?) *in the presence of ammonium chloride.* Under these conditions there is said to be a linear relationship between the calcium concentration and the soap consumption. Using a soap solution of which 1 ml. is equivalent to 1 mg. of calcium carbonate, this relationship is:

$$\text{Ca present (mg.)} = 1.14\ (\text{ml. soap solution} - 0.2)$$

Soap Solution: Shake up 100 g. pure powdered castile soap in one liter of 80% ethanol and allow to stand overnight or longer, then decant. This stock solution is 9 or 10 times as strong as the standard solution, which is prepared by suitable dilution of the stock reagent with 80% ethanol. Standardize by titrating a known quantity of calcium chloride (from calcite and hydrochloric acid, neutralized) shaking vigorously during the titration and taking the endpoint when the lather that forms will persist for 5 minutes. Make a blank correction as determined by titrating an equal volume of distilled water, and adjust the strength of the standard solution so that each ml. is equivalent to 1 mg. calcium carbonate.

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[8] V. Froboese, *Z. anorg. Chem.*, **89**, 370 (1914). See also J. Zink and F. Hollandt, *Z. angew. Chem.*, **27**, 437 (1914).

[9] J. W. Polsky and E. C. Feddern, *Ind. Eng. Chem., Anal. Ed.*, **14**, 644 (1942). Other soap titration methods for calcium in the presence of magnesium are given by E. L. Breazeale and R. A. Greene, *J. Am. Water Works Assoc.*, **30**, 1040 (1938), and W. F. Langelier, *ibid.*, **32**, 279 (1940).

[10] T. Clark, *Chem. Gaz.*, **5**, 100 (1847). American Public Health Association, *Standard Methods for the Examination of Water and Sewage*, 8th ed., New York 1936, p. 60.

Procedure: Place 50 ml. of the water sample in a 250 ml. glass-stoppered bottle and neutralize to phenolphthalein. Add 1 ml. of 10% ammonium chloride solution and 2.7 ml. of 1 N sodium hydroxide. (Variation of the p_H from 11.7 to 12.0 is said to be permissible.) The soap solution is added in small portions from a burette. After each addition shake the bottle vigorously and place on its side to observe the formation of lather. Continue the titration until the lather which forms covers the entire liquid surface and persists for a full minute. If more than 7 ml. of soap solution is required, repeat the procedure on a smaller sample diluted to 50 ml. with distilled water.

Silicate, sulfate, bicarbonate, and ferric iron in the normally encountered quantities are reported to cause no interference. It would appear, however, that buffered samples might require a different amount of alkali and that unusually high proportions of bicarbonate might better be removed before neutralization.

Titration of Barium and Determination of Sulfate: Barium may be titrated with palmitate solution as accurately as calcium and the reagent has the same titer for either of these alkaline earths. The barium titration is applicable for the rapid determination of sulfate in the absence of calcium, magnesium, and other interfering substances, or in their presence if a suitable correction is applied.

Procedure: Acidify the sulfate solution slightly with 0.1 N hydrochloric acid and measure in a known volume of barium chloride solution, in excess. Allow to stand for 10 minutes, cool, neutralize to phenolphthalein and bring back with a drop of 0.1 N acid. Titrate with palmitate solution to a permanent rose color. Titrate also the same volume of barium chloride solution and calculate the sulfate content of the sample from the difference between the two titrations. In case barium alone is being determined, subtract a blank correction of 0.3 ml., just as in the calcium determination.

Note: Quite dilute sulfate solutions may be analyzed by this procedure. The relative deviations observed with known mixtures were as follows: 100 mg. $SO_4^{=}$ per liter, 1%; 50 mg. per liter, 2%; 25 mg. per liter, 3.4%; 12 mg. per liter, 4.4%.

Salts of Other Metals: Lead salts may be titrated quantitatively with Blacher's reagent.[11] Acid solutions should first be neutralized to methyl yellow, provided that no anions of weak acids are present.

Salts of zinc or mercury are titratable the same as lead salts. Aluminum salts consume too much palmitate and fading occurs quickly after the apparent end-point. The effect is as though aluminum palmitate adsorbs alkali palmitate.

The behavior of other metal salts remains to be tested.

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[11] See H. Müller and R. Fricke, *Z. anal. Chem.*, **126,** 9 (1943).

3. Disodium Hydrogen Phosphate as Reagent.—Randall and Stevenson[12] titrate barium with a standard disodium phosphate solution, according to the reaction:

$$Ba^{++} + HPO_4^{=} \rightarrow BaHPO_4$$

The barium hydrogen phosphate has a very low solubility in nearly neutral solutions containing more than 27.5% of alcohol by volume. The disodium hydrogen phosphate solution is standardized against a known quantity of barium chloride as described below; from data given in the report it appears that slightly more disodium phosphate is required at the methyl red end-point than would be expected stoichiometrically. Randall and Stevenson recommend the method especially for rapid routine determinations of sulfate.

Procedure for Barium Titration: Neutralize the barium solution to methyl red and add one drop of 0.1 N hydrochloric acid. Introduce enough alcohol so that the mixture will contain at least 27.5% by volume at the end-point. Titrate with disodium hydrogen phosphate solution until the methyl red becomes yellow. The first yellow is not permanent; the titration is complete when the pink color no longer reappears.

Iron, manganese, copper, cadmium,[13] and other ions which form insoluble phosphates interfere. Ammonium salts must be removed, but sodium and potassium are noninterfering.

Procedure for Sulfate Determination: Acidify the approximately 0.05 M sulfate solution and stir it mechanically while adding an excess of standard 0.05 M barium chloride solution. Without filtering, neutralize to methyl red and continue as in the titration of barium. Titrate also an equal volume of the barium chloride solution and calculate the sulfate by difference. Errors of about 0.5% are to be expected, generally on the low side. Those trying this method for the first time are urged to make preliminary tests with knowns.

4. Potassium Chromate as Reagent.—The second ionization constant of chromic acid is small, about 10^{-7}, and alkali chromate solutions undergo considerable hydrolysis. Jellinek and Czerwinski[14] make use of this fact for the determination of barium and lead. The theory of this titration is discussed in Volume I, p. 64.

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[12] M. Randall and H. O. Stevenson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 620 (1942).

[13] For the titration of cadmium with disodium phosphate, see L. von Zombory and L. Pollák, *Z. anorg. allgem. Chem.*, **217**, 236 (1934).

[14] K. Jellinek and J. Czerwinski, *Z. anorg. allgem. Chem.*, **130**, 253 (1923). K. Jellinek and P. Krebs, *ibid.*, **130**, 263 (1923). S. Balachowski, *Z. anal. Chem.*, **82**, 206 (1930), recommends an adaptation of the procedure to the microtitration of barium, using bromothymol blue or phenol red as indicator. See also A. V. Ninogradov and A. E. Solev'eva, *Chem. Abstracts*, **28**, 4333 (1934).

Procedure: To the weakly acid solution of barium or lead salts add sodium hydroxide solution slowly until methyl red is just barely pink. Transfer to a white porcelain dish and titrate with standard potassium chromate solution until the supernatant liquid after settling out of the precipitate is no longer pink, but pure yellow.

Notes: (1) According to Jellinek the determination is very accurate. Kolthoff's tests indicated that the color change in the titration of barium is not sharp and is difficult to recognize. After each addition of reagent one must wait until most of the precipitate settles, so that the titration is rather lengthy. No better accuracy than to within one or two per cent was obtained, nor did the use of other indicators give better results.[15] By titrating potentiometrically with the quinhydrone electrode and working more rapidly, the errors still amounted to about 0.5%.

(2) The method fails in the presence of the anions of a weak acid.

(3) Bromothymol blue serves well as indicator in the titration of lead salts with chromate.

5. Potassium Cyanide as Reagent.—A solution of potassium cyanide reacts strongly alkaline to phenolphthalein because of hydrolysis, hence it may be used for titrating metals which form neutral cyanides; the presence of excess reagent is revealed by an increase in hydroxyl-ion concentration. An alkali cyanide to be used for titration purposes must be pure and free from alkali. The solution may be standardized by titration with acid to methyl orange, by the Liebig-Dénigès method (p. 282), or against a standard solution of the metal salt being determined.

Determination of Mercuric Salts: Mercury cyanide is ionized so slightly in aqueous solution that no hydrolysis of cyanide ion can be detected. Rupp[16] and his associates made use of this fact for the determination of mercuric salts. The solution of the salt must contain no excess of free acid. Since mercuric salts themselves react acid because of hydrolysis, an excess of alkali chloride is added; the solution is tested with methyl yellow or methyl orange and is neutralized if necessary. The liquid is then treated with an excess of standard potassium cyanide solution and the latter is titrated back to the same indicator:

$$HgCl_2 + 2CN^- \rightleftarrows Hg(CN)_2 + 2Cl^-$$

While mercuric chloride can be titrated directly with potassium cyanide using phenolphthalein as indicator, the titration is successful only with solutions more concentrated than about 0.5 N. In solutions of high alkali chloride content the above reaction does not proceed quantitatively to the right and the color change becomes less sharp. The back titration to methyl orange gives good results even in this case. According to Jellinek and Krebs[17] one is subject to an error of about 3% in the direct titration of mercuric chloride with potassium cyanide; this error is independent of the dilution. Why these investigators carried out the titration at boiling is not readily apparent.

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[15] *Cf.* A. A. Briwul, *Z. anorg. allgem. Chem.*, **156,** 210 (1926). Briwul found even greater deviations; he improved the procedure by using a suitable reference solution and applying a correction.

[16] E. Rupp, *Chem.-Ztg.*, **32,** 1077 (1908).

Morawitz[18] states that the reaction between mercuric chloride and cyanide takes place very slowly in dilute solution, wherefore the end-point in the direct titration appears too soon. According to him hydrogen ions accelerate the reaction; he recommends adding several drops of 0.02 N hydrochloric acid as a catalyst and titrating to a yellow color with *p*-nitrophenol. The procedure is reported to be accurate even with 0.01 N solutions. A correction is applied for the quantity of acid originally introduced. This method has not yet been sufficiently tested; a thorough study of the p_H changes during the titration would be desirable. In any event, the potassium cyanide solution employed should be free of excess alkali or carbonate.

6. Aluminum Chloride and Cerous Nitrate as Reagents for Fluoride.—As has already been mentioned (p. 111), fluoride combines with an aluminum salt to form a stable complex which is neutral in aqueous solution:

$$6F^- + Al^{+++} \rightleftarrows AlF_6^{\equiv}$$

If one titrates a neutral fluoride solution with an aluminum salt, hydrolysis of the first excess of the latter causes the system to react acid. Kurtenacker and Jurenka[19] based a volumetric method for fluoride ions on this reaction.

Procedure: The solution is neutralized to phenolphthalein and enough neutral sodium chloride is introduced to saturate it. After addition of some methyl red, the mixture is heated to 70° or 80°C. and titrated with 0.16 M aluminum chloride solution until the yellow color changes to pink. The color change under these conditions is very sharp. With more dilute solutions the end-point remains distinct enough so that 3 mg. of fluoride, for example, may be determined to within 0.2 to 0.3 mg.

Titration at room temperature is also possible if the aluminum solution is added very slowly (one drop per second). With more rapid addition the end-point appears too soon. In hot solution the result is independent of the titration rate.

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[17] K. Jellinek and P. Krebs, *Z. anorg. allgem. Chem.*, **130**, 318 (1923).

[18] H. Morawitz, *Z. anorg. Chem.*, **60**, 457 (1909).

[19] A. Kurtenacker and W. Jurenka, *Z. anal. Chem.*, **82**, 210 (1930).

The aluminum chloride solution should contain no free acid or basic salt as shown by a test with excess fluoride (p. 111). Its effective strength is established through titration of a standard alkali fluoride solution.

Notes: (1) According to Kurtenacker and Jurenka the strength decreases during storage, without outward evidence of such change and without alteration of the gross aluminum content. The decrease may amount to about 6 or 8% within two weeks after preparation and thereafter the titer stays nearly constant. If the solution is boiled during preparation, the smaller strength is obtained at once and subsequently remains unchanged. The reason for this singular behavior is not clear; possibly a colloidal hydrolysis product of the aluminum chloride is formed on boiling or aging. It is not disclosed whether potassium alum, which is not so suitable for titrating strong fluoride solutions because of its lower solubility (about 0.1 M at 15°C.), behaves in the same way.

(2) The procedure has limited applicability because of many interferences. Cations which form complex or insoluble fluorides must naturally be absent. While traces of silicic acid may have no influence on the result, larger quantities must be removed. Nitrate, chloride, and sulfate do not interfere; phosphate, borate, and carbonate, as well as all anions which give insoluble or complex aluminum salts, render the determination impossible.

Kurtenacker and Jurenka gave also a method for determining fluoride with standard cerous nitrate solution. The neutral fluoride solution is heated to 80°C. and titrated to a pink color with methyl red; cerous fluoride precipitates during the titration. Deviations of up to 4% from the theoretical titer were reported. It is possible that the cerous nitrate employed was not entirely pure. In contrast, Batchelder and Meloche[20] obtained excellent results by the same procedure. Using a stock solution containing 4.01 g. of cerous nitrate per liter, they found deviations of 0.2–0.4 mg. in titrating 30–150 mg. quantities of sodium fluoride with a macroburette, and of 0.04–0.14 mg. in titrating 0.3–0.7 mg. with a microburette. Sulfate, oxalate, phosphate, and other ions which form complexes or slightly soluble compounds with cerium or fluoride interfere.

Batchelder and Meloche note that the methyl red behaves in this case somewhat as an adsorption indicator rather than as a simple acid-base indicator. A solution containing less than 2.5 ml. of cerous nitrate solution and no fluoride remains yellow, whereas addition of less than the equivalent amount of fluoride brings about a slow change to red. At the equivalence-point (slight excess of fluoride) the color returns to yellow and the change is reversible from this point on. In other words, the precipitated cerous fluoride adsorbs the red form of methyl red in the presence of excess cerous ions and the yellow form when fluoride predominates.

Ampho-magenta, an azo dye available from the National Aniline and Chemical Company, was also found to be a good adsorption indicator for the titration. This indicator is made up as an 0.1% solution in water and 1 ml. is used per 50 ml. of liquid to be titrated. The neutral fluoride solution containing ampho-magenta is titrated at room temperature with cerous nitrate; at the equivalence-point the color changes from deep blue to a less intense purple. Under the best conditions the error amounts to about ±0.1 mg. of sodium fluoride.

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[20] G. Batchelder and V. W. Meloche, *J. Am. Chem. Soc.*, **53**, 2131 (1931); **54**, 1319 (1932).

Henne and co-workers[21] made use of cerous nitrate for the titration of fluoride liberated from organic substances. They improved the end-point by use of a methyl red–bromocresol green mixed indicator.

An extensive study of the cerous nitrate titration was contributed by Nichols and Olsen,[22] who employed it for determining organic fluorides after decomposition with sodium peroxide in a nickel Parr microbomb. They found the magnitude of the p_H change at the end-point to be affected greatly by high concentrations of sodium nitrate but were able to secure useful results in 1 M sodium nitrate solution. Sodium halides behave similarly. If more than 2 mg. of sodium sulfate is present the end-point cannot be detected; therefore the method cannot be used for the analysis of sulfur-containing materials. Interference is also caused by buffering agents, or by the presence of more than 0.04 g. of sodium perchlorate per 10 ml.

In agreement with Kurtenacker and Jurenka,[19] the above authors found an improved p_H change at higher temperature. The change is even more pronounced if the titration is carried out in 50% ethanol, at about 90°C. Under these conditions, however, the reaction is not stoichiometric. The cerous nitrate solution must be standardized against fluoride under the same circumstances that prevail during titration of an unknown.

Procedure of Nichols and Olsen: The titration is best performed in a double flask made by joining two 200 ml. round-bottom Pyrex flasks just below the necks, with a short, curved piece of glass tubing. This permits pouring the solution back and forth between the flasks. Probably the use of two beakers would serve the purpose, though less conveniently. Since the color change is rather delicate, comparison is made in front of a flashed opal screen illuminated by a daylight lamp.

Prepare the sample so that the inorganic fluoride is present in 10 ml. of nearly neutral solution, in one side of the double flask. Add an equal volume of 95% ethanol and 3 drops of 0.02% cresol red solution. Adjust with 0.1 N alkali to a definite pink color and bring to a gentle boil, then add 1 or 2 drops of 0.1 N nitric acid in excess and boil again to expel all carbon dioxide, as shown by the solution remaining yellow. Adjust to a very faint pink color with 0.001 N alkali.

Introduce 2 drops of a saturated alcoholic solution of methyl red and 1 drop of 0.04% bromocresol green. The resulting color should be a clear green. Titrate dropwise with 0.01 N cerous nitrate, boiling and agitating the solution frequently. When the color becomes a light orange, divide the mixture between the two flasks and to one part add another drop of reagent, noting the color difference. Reunite the portions, mix, divide equally, and repeat the addition of a drop, continuing in this manner until the maximum color difference is observed. Some experience with the procedure may be necessary before the end-point can be located precisely.

Frere[23] employs yttrium nitrate as a reagent for the titration of fluoride with methyl red as indicator. He mentions that the end-point with yttrium

[21] D. M. Hubbard and A. L. Henne, *J. Am. Chem. Soc.*, **56**, 1078 (1934) (decomposition of volatile organic fluorides by combustion). E. W. Scott and A. L. Henne, *Ind. Eng. Chem., Anal. Ed.*, **7**, 299 (1935) (ashing of organic matter with calcium oxide, followed by distillation as described on p. 324).

[22] M. L. Nichols and J. S. Olsen, *Ind. Eng. Chem., Anal. Ed.*, **15**, 342 (1943).

[23] F. J. Frere, *Ind. Eng. Chem., Anal. Ed.*, **5**, 17 (1933).

reagent is sharper when the concentration of fluoride is large, while the end-point with cerous solution is preferable for small concentrations. The standard solution is prepared by dissolving 16 g. of $Y(NO_3)_3 \cdot 4H_2O$ in a liter of water, boiling for 2 or 3 minutes, allowing to stand overnight and filtering. It is standardized against a known solution of sodium fluoride containing approximately the same quantities of salts as are expected in the unknown solutions. The titration is performed at room temperature, after preliminary neutralization of the solution to phenolphthalein. Carbonate must first be removed, as must sulfate if present in an amount of more than 0.1 g. per 100 ml.

7. Other Reagents.—***Mercuric Perchlorate:*** The common mercuric salts of oxygen acids are generally ionized and strongly hydrolyzed in aqueous solution. Thus an 0.1 N solution of mercuric perchlorate has a hydrogen-ion concentration of about 0.03 N. Mercuric halides, on the other hand, are very slightly dissociated and one can therefore make use of mercuric perchlorate as a reagent for the titration of chloride or bromide. The standard solution must contain no excess of free acid; in this respect mercuric perchlorate is superior to the nitrate, which easily decomposes in water to form a basic salt and free nitric acid.

Preparation of Reagent: A standard solution may be prepared from pure crystallized mercuric perchlorate or by shaking a perchloric acid solution with excess mercuric oxide until saturated. The reagent is tested for neutrality by treating a portion of it with an excess of pure sodium chloride and adding a little methyl yellow; the indicator should show its water color. The solution should be kept in a bottle of good glass which will not liberate alkali. Standardization may be made against a known thiocyanate solution (p. 337) or against pure sodium chloride as in the procedure. Methyl orange is better suited here than methyl yellow.

Procedure: Neutralize the alkali chloride solution to methyl orange and titrate with mercuric perchlorate until the color changes to a definite orange-red (p_T about 3.6).

Bromide and thiocyanate may be titrated similarly.

Notes: The results are accurate to within about 0.5%. No detailed study of the method has been published; the author encountered the difficulty that upon standing the reagent solution yields an excess of free acid. Under these conditions the end-point appears too soon. One should therefore always test for neutrality. If free acid is found, several drops of 0.1 N alkali may be added to the sample and a corresponding correction applied to the titration.

Sodium Sulfide: The second ionization constant of hydrogen sulfide is very small and solutions of the normal alkali sulfides react strongly alkaline. It might therefore be expected that hydrolytic precipitation titrations of various metals which form insoluble sulfides could be carried out with sodium sulfide. Three difficulties stand in the way of this procedure, however:

(*a*) Most sulfides are dark in color and interfere with observation of the end-point.

(*b*) The compositions of many of the precipitates obtained with sodium sulfide are variable.

(*c*) Sulfide solutions are easily oxidized by the air.

According to Jellinek and Krebs[24] the titration of zinc with sodium sulfide gives useful results, in the analysis of zinc alloys, for example. They employ a 0.1 N sulfide solution standardized against 0.1 N hydrochloric acid with methyl orange. The authors prefer to start with pure sodium sulfide, which can easily be prepared by the method of Böttger:[25]

50 g. of coarsely crushed sodium hydroxide is dissolved in 200 g. of alcohol under an atmosphere of dry hydrogen, in a flask fitted with a reflux condenser. The solution is filtered and divided into two equal parts, one of which is saturated with hydrogen sulfide. White crystals appear during the saturation process but redissolve when all of the alkali is converted to sodium hydrosulfide. The other portion is now added to this in a closed cylinder, whereupon the normal sulfide is precipitated. It is dissolved by warming to 90°C. and then recrystallized by cooling. The crystals are pressed between sheets of filter paper and are dried for a very short time over sulfuric acid. The drying must not be prolonged or the product, $Na_2S \cdot 5H_2O$, will lose part of its water of hydration. Standard sulfide solutions must be protected against air oxidation.

Zinc Titration: Neutralize the zinc salt solution to methyl red, adjusting just to the red color, and titrate with standard sodium sulfide solution to a permanent yellow. Toward the end the red color returns within a few seconds after the first change to yellow, and more sulfide has to be added. According to Jellinek and Krebs the final end-point is sharp and the result can be accurate to within about 0.2%.

Notes: (1) Poor results are obtained if the zinc concentration is originally below 0.01 N.

(2) Naturally many other metals interfere and would have to be removed if present. On this account the procedure does not have much practical usefulness.

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[24] K. Jellinek and P. Krebs, *Z. anorg. allgem. Chem.*, **130**, 309 (1923).

[25] H. Böttger, *Ann.*, **223**, 335 (1884).

Lead Nitrate: Titrations of the alkali salts of various anions with a standard solution of lead nitrate are described by Ringbom[26] and by von Zombory and Pollák.[27] Since these are of limited applicability, they are mentioned here merely for the sake of completeness:

Carbonates are titrated very slowly in hot solution, to a p_T of 7.2 with phenol red indicator. *Oxalates* are first neutralized to a p_H of 8 to 8.5 and then titrated using phenol red[26] or chlorophenol red.[27] *Sulfates* cannot be determined accurately even in the presence of 20% ethanol. *Sulfites* may be determined to within about 1% with bromocresol purple as indicator; good results for *chromate* are obtained in the same way (see also p. 319). *Tungstates* are brought to a p_H of 8.5 to 9 and are titrated hot using bromothymol blue as indicator. *Molybdates* are adjusted initially to from 9 to 9.5 and phenol red is employed; the accuracy is stated to be within 0.2 to 0.5%.

[26] A. Ringbom, *Thesis*, Åbo, Finland 1934; *Chem. Abstracts*, **29**, 3261 (1935).

[27] L. von Zombory and L. Pollák, *Z. anorg. allgem. Chem.*, **217**, 237 (1934).

CHAPTER VII

SPECIAL METHODS OF ACIDIMETRY AND ALKALIMETRY

This chapter is devoted to methods, which, though they involve acid-base reactions, are not conveniently classified within groups that have been discussed in the preceding chapters.

1. Methods Based on Formation of Mercuric Complexes.—(*a*) ***The Cyanide Complex:*** Mention has already been made (p. 197) of the determination of mercuric ions by reaction with cyanide to form a complex. This reaction may also be applied for the direct titration of mercuric salts or of hydrogen cyanide, with sodium hydroxide:

$$HgCl_2 + 2HCN \rightleftarrows Hg(CN)_2 + 2HCl$$

Procedure for Titrating Mercuric Salts: Prepare a solution of the salt, containing no excess of free acid, and add to it slightly more than the equivalent quantity of hydrocyanic acid. Titrate the liberated strong acid with standard alkali to the water color of methyl yellow, then add a little more hydrocyanic acid. If the color does not change, the end-point has been reached.

Notes: (1) This method was originated by Andrews[1] and has since been described anew by others. Andrews used *p*-nitrophenol, which is a less satisfactory indicator than methyl yellow. Kolthoff and Keijzer[2] obtained excellent results with the above procedure and recommended it for the analysis of mercuric chloride alone or in various preparations.

(2) The hydrocyanic acid solution is conveniently prepared by titrating potassium cyanide with hydrochloric acid, using methyl yellow as indicator.

(3) The neutrality of a mercuric salt solution may be tested by adding methyl yellow and an excess of alkali chloride. If no free acid is present, the reaction remains neutral after addition of the alkali chloride.

Procedure for Titrating Hydrogen Cyanide: Neutralize the sample to methyl yellow and introduce an excess of a solution 0.25 M in mercuric chloride and 0.5 M in sodium chloride, then titrate with standard alkali to the water color of methyl yellow. After the change add a little more sodium mercuric chloride solution to make sure that the reaction has gone to completion.

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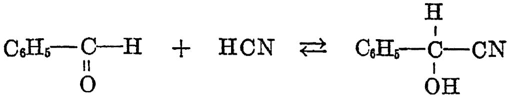
[1] L. W. Andrews, *Am. Chem. J.*, **30**, 187 (1903).

[2] I. M. Kolthoff and J. Keijzer, *Pharm. Weekblad*, **57**, 914 (1920).

Notes: (1) The determination can be made with good accuracy and various applications are possible. In the assay of potassium cyanide containing free alkali or alkali carbonate, one first determines the sum of cyanide and free alkalinity by titration to methyl yellow, with standard acid. Then an excess of sodium mercuric chloride is added and the liberated acid, equivalent to cyanide alone, is titrated with alkali. Free alkalinity is given by the difference between the two titrations.

(2) The methods are suitable also for determination of the free hydrocyanic acid in preparations of bitter almond oil, "oleum amygdalarum."[2] Part of the cyanide in such liquids is bound by benzaldehyde:



$$C_6H_5-\underset{\underset{O}{\|}}{C}-H \quad + \quad HCN \quad \rightleftarrows \quad C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CN$$

In acid solution the equilibrium is approached very slowly. If one first brings the sample to the water color of methyl yellow, then adds several milliliters of sodium mercuric chloride solution, only the free hydrocyanic acid reacts and the liberated acid may be titrated directly with alkali. The procedure gives excellent results.

Total cyanide can also be determined easily. One treats 25 ml. of the solution with about 5 ml. of 0.2 N sodium mercuric chloride and 10 ml. of 0.1 N sodium hydroxide, so that the reaction becomes strongly alkaline to phenolphthalein. After 15 minutes, one titrates the excess alkali to methyl yellow. Under these conditions both the free and bound cyanide are converted into mercuric cyanide.

(*b*) ***Other Complexes:*** Ions such as thiosulfate and the halides also yield slightly dissociated or complex compounds with mercuric ions. The complex, $HgI_4^{=}$, formed upon addition of an alkali iodide, is very stable. An application of this has been made in the use of mercuric oxide for standardizing acids (p. 90). A similar procedure may be employed for the determination of several mercury compounds.

Mercuric Oxide: Dissolve a weighed quantity of the sample in a little water containing an excess of potassium iodide or bromide and titrate with hydrochloric acid to methyl yellow. For 0.1 g. of oxide, 0.5 g. of iodide or 2 g. of bromide is sufficient. Phenolphthalein may be used as indicator if carbon dioxide is excluded.

Mercuric Cyanide[3]*:* Dissolve 0.25 g. in water, add 2 g. of potassium iodide and titrate the liberated potassium cyanide with standard acid, to methyl yellow. This procedure gives good results.

Notes: (1) The iodide complex of divalent mercury is more stable than the cyanide complex. Furthermore, during titration the cyanide ions are removed as slightly dissociated hydrocyanic acid, so that equilibrium in the following equation is shifted strongly to the right:

$$Hg(CN)_2 + 4I^- \rightleftarrows HgI_4^{=} + 2CN^-$$

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[3] E. Rupp, *Chem.-Ztg.*, **32**, 1088 (1908).

(2) The thiosulfate complex is also quite stable. Rupp and Müller[4] substitute 2 g. of pure sodium thiosulfate for potassium iodide and titrate in the same way. This procedure is reliable for the analysis of preparations free from other basic mercuric compounds. The reaction appears to be as follows:

$$Hg(CN)_2 + 2S_2O_3^{=} \rightleftarrows Hg(S_2O_3)_2^{=} + 2CN^-$$

Basic Mercuric Cyanide: According to Holdermann[5] the oxide content of mercuric oxycyanide, $Hg(CN)_2 \cdot HgO$, can be determined easily by titrating with acid in the presence of chloride:

$$HgO + 4Cl^- + H_2O \rightleftarrows HgCl_4^{=} + 2OH^-$$

The mercuric cyanide is not affected, being much less dissociated than complex mercuric chloride. Rupp[4] has extended the method to allow determination of the mercuric cyanide content also. To 0.3 g. of basic mercuric cyanide (oxycyanide) are added 40 to 50 ml. of warm water and 0.5 g. of sodium chloride. After cooling one adds 2 or 3 drops of methyl orange or methyl yellow and titrates with 0.1 N hydrochloric acid to the first deviation from the water color. This titration represents mercuric oxide; to determine cyanide one next adds 1.5 to 2 g. of pure sodium thiosulfate and titrates again in the same way. The procedure gives accurate results.

Vieböck[6] makes use of a saturated solution of basic mercuric cyanide for the determination of alkali chloride or bromide. An excess of this reagent is added to the neutral halide solution and the liberated alkali is titrated with standard sulfuric acid to methyl red:

$$Hg(CN)_2.HgO + 2Cl^- + H_2O \rightleftarrows Hg(CN)_2.HgCl_2 + 2OH^-$$

In determining chloride one should employ as comparison solution a mixture of reagent and a quantity of hydrochloric acid about equivalent to the alkali chloride expected. No reference liquid is needed for bromide determinations.

Commercial mercuric oxycyanide may be crystallized once from water and dissolved without drying (the dry salt is explosive). The saturated solution, containing about 20 g. per liter, should be kept in a dark bottle. 10 ml. of this solution upon treatment with 0.2 ml. of 0.01 N sulfuric acid should react definitely acid to methyl red.

Ingram[7] has applied the method to micro halogen titrations and indirectly to the determination of sulfuric acid, formed by combustion of organic sulfur compounds, after precipitation with standardized barium chloride. The excess of the latter is titrated as has been described.

Mercuric Aminochloride: Complex formation with iodide or thiosulfate may be applied to the assay of mercuric aminochloride, $HgNH_2Cl$, the so-called "white precipitate." Rupp and Lehmann[8] dissolve 0.2–0.3 g. of the substance and 2 g. of potassium iodide in about 50 ml. of water, in a closed flask. When all is in solution, the total ammonia and potassium hydroxide are titrated to methyl yellow:

$$HgNH_2Cl + 4I^- + H_2O \rightleftarrows HgI_4^{=} + Cl^- + NH_3 + OH^-$$

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[4] E. Rupp and K. Müller, *Apoth.-Ztg.*, **40**, 539 (1925). E. Rupp, *Pharm. Zentralhalle*, **67**, 145 (1926).

[5] K. Holdermann, *Arch. Pharm.*, **243**, 600 (1905).

[6] F. Vieböck, *Ber.*, **B65**, 496 (1932).

[7] G. Ingram, *Analyst*, **69**, 265 (1944).

[8] E. Rupp and F. Lehmann, *Pharm.-Ztg.*, **52**, 1014 (1907).

1 ml. of 0.1 N acid corresponds to 12.60 mg. of mercuric aminochloride. Accurate results can be obtained.

It is also possible to work with thiosulfate in place of iodide. One dissolves 0.2–0.3 g. of sample and 2–3 g. of pure sodium thiosulfate in 30 ml. of water and titrates in the same way. The white precipitate dissolves very rapidly in thiosulfate solution.

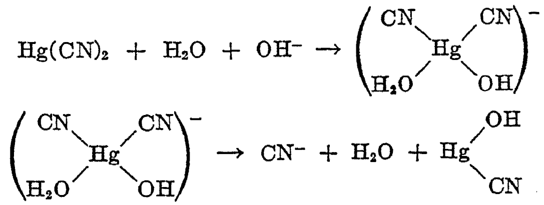
If a more specific mercury determination is required, one may dissolve mercuric aminochloride in a slight excess of potassium cyanide solution[9] (the quantity of cyanide taken need not be known accurately) and neutralize to methyl yellow. Under these conditions all the mercury is bound as cyanide. Then 2 g. of potassium iodide or sodium thiosulfate is added and the liberated alkali is titrated as described on p. 205.

Mercuric Chloride: Skramovsky and Uzel[10] determine mercuric chloride by converting it to aminochloride and applying the foregoing titration of Rupp and Lehmann. The white precipitate may occur in various forms including $HgNH_2Cl$, $Hg(NH_2)_2Cl_2$, or $HgO \cdot HgNH_2Cl$, depending upon the composition of the solution, but in any case two milliequivalents of alkali are liberated per millimole of mercury.

To a measured amount of about 0.1 N mercuric chloride solution add 3 ml. of 10% ammonia and 5 ml. of 0.5 N sodium hydroxide. Boil for 1 minute, cool, add a few drops of methyl red, and neutralize carefully, partly with 1 N sulfuric acid and finally with 0.1 N, until the pink color will remain for several seconds. Then add 2 g. of potassium iodide and titrate the liberated alkali to methyl red.

Note: Boiling with alkali is necessary in order that the precipitate shall assume a compact form, not easily attacked during subsequent neutralization or by the presence of nitrates or halides, which otherwise would cause low results. Though no mention of carbonate interference is made, it would appear wise to work with carbonate-free alkali and ammonia.

Silver: Mercuric cyanide in aqueous solution is practically undissociated; the cyanide-ion concentration is so small that no precipitate is given with silver nitrate. However, if a trace of alkali is added to a silver nitrate–mercuric cyanide mixture, a turbidity appears immediately. In fact, the system is so sensitive to hydroxyl ions that it serves as a turbidity indicator for p_H 4.2; a complex is formed:



$$Hg(CN)_2 + Ag^+ + OH^- \rightarrow Hg(OH)(CN) + AgCN$$

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[9] I. M. Kolthoff, *Pharm. Weekblad,* **55,** 208 (1918).

[10] S. Skramovsky and R. Uzel, *Collection Czechoslov. Chem. Commun.,* **6,** 435 (1934).

Feigl and Tamchyna[11] have developed an acidimetric method for silver, making use of this behavior. The silver (nitrate) solution is neutralized to methyl red and treated with a small excess of 2% aqueous mercuric cyanide. In consequence of the behavior mentioned above, the p_H becomes 4.2. The mixture is titrated with 0.1 N sodium hydroxide to a yellow color, each mole of alkali corresponding to one mole of silver nitrate.

Note: Thallium causes no interference, even in large amounts. If lead is present an excess of sodium sulfate should be added to the neutral solution before introduction of mercuric cyanide. Filtration is unnecessary.

2. Methods Based on Precipitation of a Sulfide.—***Determination of Zinc:*** When the zinc salt of a strong acid is treated in neutral solution with hydrogen sulfide, zinc sulfide precipitates and the liberated acid may be titrated:

$$Zn^{++} + H_2S \rightarrow ZnS + 2H^+$$

In principle the mercury determination with hydrocyanic acid and alkali (p. 204) is entirely similar, aside from the fact that the undissociated compound formed is soluble in one case and insoluble in the other. This method for zinc was described originally by Taylor[12] and later by Houben.[13] It is noteworthy that both authors arrived independently at nearly the same procedure. The method is seldom used, however, partly because of the objectionable characteristics of hydrogen sulfide.

Procedure: The zinc salt solution, which should not be stronger than about 0.5 N, is neutralized to methyl orange and hydrogen sulfide is passed through for half an hour. Then 20–30 mg. of ferrous sulfate, but no more, is introduced and the mixture is titrated with standard borax (see Note 2), meanwhile being shaken vigorously. The end-point is shown by a change to light chocolate-brown or a "coffee and cream" color.

Notes: (1) When all the free acid has been neutralized, ferrous sulfide or, more correctly, a double sulfide of zinc and iron, precipitates. This double sulfide may also be formed too early, by local excesses of reagent, and thus may cause some difficulty with the end-point.[14] The change is not reversible.

(2) If the titration is made with sodium hydroxide, results about 3–4% low are obtained. With borax solution the error is only about 1%. Sodium carbonate may also be used.

(3) Most attempts to apply the usual acid-base indicators have been unsuccessful because the color change is very poor unless the solution is filtered. On the other hand, filtration is barred since zinc sulfide adsorbs an appreciable

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[11] F. Feigl and J. Tamchyna, *Ber.*, **B62**, 1897 (1929).

[12] J. M. Taylor, *J. Soc. Chem. Ind.*, **28**, 1294 (1909).

[13] J. Houben, *Ber.*, **52**, 1613 (1919).

[14] I. M. Kolthoff and J. C. van Dijk, *Pharm. Weekblad*, **58**, 538 (1921).

quantity of acid. The titration of a filtered solution may give results low by 3 or 4%.

Iodoeosin may be used as indicator with some success. After passing the gas through, one adds 10 drops of 0.1% iodoeosin in alcohol, plus enough ether to form a good layer. The titration is carried to a point at which a red color appears in the ether layer and remains even after thorough shaking. Emulsions formed during the shaking may be broken by adding a few drops of alcohol. With some practice, results accurate to within 0.5% are possible. An advantage of this method is that the color change is reversible.

(4) Lead, copper, bismuth, and other elements which form insoluble sulfides in acid or nearly neutral solutions must be removed beforehand. Manganese does not interfere; neither do cobalt, nickel, or aluminum in amounts below 10% of the zinc, according to Taylor.[12]

3. Determination of Persulfate.—Solutions of persulfate decompose upon heating:

$$S_2O_8^{=} + H_2O \rightarrow 2SO_4^{=} + 2H^+ + O$$

According to Tarugi[15] the decomposition is complete after 20 minutes of boiling; other workers[16] have stated that up to 35 minutes may be required. Palme[17] found an even longer time to be necessary in the case of pure potassium persulfate. Kurtenacker and Kubina[18] confirmed Palme's finding and proposed a method for the determination of alkali persulfates, in which silver nitrate is introduced as a catalyst.

Procedure: Dissolve about 0.4 g. of the persulfate in water, neutralize to methyl red or methyl orange, add 10 ml. of 0.1 N silver nitrate, and bring to a volume of about 100 ml. Boil gently for 10 minutes in a flask bearing a small funnel in the neck, then cool the solution, and titrate with 0.1 N alkali to the same indicator. If the persulfate solution has a larger volume, longer boiling may be necessary (20 minutes for 200 ml.).

The foregoing method is not applicable to the analysis of ammonium persulfate, or of other persulfates in the presence of ammonium salts, since partial oxidation to nitric acid takes place and high results are obtained. Therefore van der Meulen[19] makes use of a reaction with hydrogen peroxide:

$$S_2O_8^{=} + H_2O_2 \rightarrow 2SO_4^{=} + 2H^+ + O_2$$

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[15] N. Tarugi, *Gazz. chim. ital.*, **32, II,** 383 (1902); *Chem. Zentr.*, **74, I,** 616 (1903).

[16] C. Marie and L. J. Bunel, *Bull. soc. chim.*, **29,** 930 (1903). M. G. Levi and E. Migliorini, *Gazz. chim. ital.*, **36, II,** 599 (1906); *Chem. Zentr.*, **78, I,** 322 (1907).

[17] H. Palme, *Z. anorg. allgem. Chem.*, **112,** 102 (1920).

[18] A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, **83,** 14 (1931).

[19] J. H. van der Meulen, *Rec. trav. chim.*, **51,** 445 (1932).

No oxidation of ammonia occurs in this system. However, the excess peroxide interferes by reacting with silver ions during titration, unless the latter are removed as silver chloride or by binding as a complex. In the following generalized procedure an ammonium salt is added to react with silver at the end-point; manganous ions are also introduced, thereby further shortening the boiling time.

Procedure of van der Meulen: To 50 ml. of an approximately 0.1 N persulfate solution, previously neutralized if necessary, add 20 ml. of neutral 1 N hydrogen peroxide, 5 ml. of 0.1 N silver nitrate, and 2 ml. of 0.1 M manganous sulfate. Warm on a steam bath until the main reaction (oxygen evolution) is finished, then boil gently for 5 minutes. Cool, add 2 g. of neutral ammonium sulfate or nitrate, and titrate with 0.5 N alkali to the pure yellow color of methyl orange.

4. Determination of Water and Alcohols.—A number of volumetric methods for water and alcohols have been based upon their reactions with other substances, generally organic, to form acids which may be titrated. These procedures for water are not of so much importance now as they were before introduction of the Karl Fischer iodometric method; nevertheless, several of them are described in this section. The Fischer procedure and its applications will be presented in Volume III.

(*a*) ***Reaction with Acetyl Chloride and Pyridine:*** Smith and Bryant[20] have introduced methods based upon the following reactions, carried out in the presence of pyridine:

$$CH_3COCl + H_2O \rightarrow HCl + CH_3COOH$$
$$CH_3COCl + ROH \rightarrow HCl + CH_3COOR$$

Two equivalents of titratable acid are liberated for each mole of water, but only one for each mole of alcohol. This difference permits determination of either water or alcohols, in organic media.

Reagents: Acetyl chloride solution, 1.5 moles (about 118 ml.) of pure acetyl chloride diluted to one liter with dry, c.p. toluene.

Pyridine, dry, c.p. grade material.

Ethanol, absolute (needed for water determination only).

Sodium hydroxide, 0.5 N standard solution, in water.

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[20] D. M. Smith and W. M. D. Bryant, *J. Am. Chem. Soc.*, **57**, 61 (1935) (alcohols); **57**, 841 (1935) (water).

Procedure for Determination of Water: Using a Lowy automatic pipette, or other suitably protected measuring apparatus, place 10 ml. of 1.5 M acetyl chloride solution in a dry 250 ml. glass-stoppered volumetric flask. Place the flask in a beaker of finely chopped ice and allow to stand for a minute or two before adding 2 ml. of pyridine from a pipette. Stopper and shake. Introduce the weighed or measured sample, in amount sufficient to react with only about two-thirds of the acetyl chloride (0.18 g. of water, or less if alcohols are also present). Shake vigorously, allow to stand for at least 2 minutes at room temperature, then pipette in 1 ml. of absolute ethanol and shake thoroughly again. After 5 minutes, pipette in 25 ml. more of the ethanol. Let stand for 10 minutes longer before titrating with 0.5 N alkali to phenolphthalein.

Run a blank determination in the same way. The increase in acidity of the sample over the blank is a direct measure of the water present, each millimole of difference representing one millimole of water.

Note: In experiments on *n*-propanol–water mixtures, Smith and Bryant found the results to be reproducible within ±1% when 50 mg. or more of water was taken; under these conditions also their titrations accounted for 97 to 98% of the water. An empirical correction may be determined and applied to compensate for the average error occurring with a given substance.

As little as 2 mg. of water may be detected. In the case of inert solvents such as hydrocarbons, ethers, esters, and ketones, samples of up to 10 g. may be used, so that 0.02% moisture is detectable. Only 1 g. of an alcohol or of most other reactive materials should be taken. With methanol, glycol, or glycerol, the amount of sample should be limited to 0.5 g.

Formic acid interferes, but most other fatty acids do not if their titers are taken into account. Organic bases which are strong enough to affect phenolphthalein interfere; weaker bases do not. Substances that hydrolyze easily, such as the lower esters of formic acid, are objectionable. The same is true of aldehydes, which cause the end-point to fade quickly.

The purpose of adding the ethanol in two steps is to prevent interference from traces of moisture in this solvent. The first milliliter serves to decompose acetyl chloride, after which no further reacton occurs. The rest of the alcohol is added merely as a solvent and presumably might be replaced by a cheaper substance.

Procedure for Determination of Alcohols: Follow the same procedure as for water determination (above) up to the point at which the sample is introduced. Use an amount of sample which will react with not more than two-thirds of the acetyl chloride; solid samples may be washed in with 5 ml. of toluene. Shake the mixture and place the flask in a water bath at 60 ± 1°C., loosening the stopper momentarily to allow for air expansion. Then stopper tightly, keep in the bath for 20 minutes with occasional shaking, remove, and cool in ice water.

Add 25 ml. of water to decompose the excess reagent, shaking vigorously to complete the reaction in each phase. Titrate with 0.5 N alkali to phenolphthalein. Carry a blank through the same procedure. The decrease in acidity of the sample as compared with the blank is proportional, mole for mole, to the amount of alcohol or reactive hydroxyl groups present.

Note: Not more than a few per cent of moisture should be present, since water decomposes the reagent. No interference is caused by a trace, however.

Good results for a number of alcohols and phenols are reported by Smith and Bryant. Unfortunately, they worked with unpurified compounds in several cases, so that, for example, results of 95.8% and 93.1% are given for assays of phenol and *o*-cresol, respectively. Where comparisons were made with results by the acetic anhydride–pyridine method of Marks and Morrell,[21] the agreement was excellent (±0.5%).

Benzoin and glucose react incompletely, probably because of their slight solubilities. Tertiary alcohols react very incompletely. Interference is caused by amines, mercaptans, higher fatty acids, and easily hydrolyzed esters, also by large amounts of aldehydes. Ketones interfere slightly but corrections for their effects may be found easily through experiments on known mixtures.

(*b*) ***Reaction with Acetic Anhydride and Sodium Methylate:*** Toennies and Elliott[22] base their method for determining water and alcohols on the acid-catalyzed reactions with acetic anhydride and sodium methylate in organic media:

$$(CH_3CO)_2O + OCH_3^- \rightarrow CH_3COOCH_3 + CH_3COO^- \tag{1}$$

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH \tag{2}$$

$$2CH_3COOH + 2OCH_3^- \rightarrow 2CH_3OH + 2CH_3COO^- \tag{3}$$

Acetic anhydride can be titrated according to reaction (1) with a solution of sodium methylate in methanol, to thymol blue as indicator. However, if water is present the acetic anhydride is hydrolyzed and twice as much methylate is required (reactions 2 and 3). In dilute solution in acetonitrile, reaction (2) is extremely slow, but is markedly catalyzed by acids. Toennies and Elliott prefer 2,4-dinitrobenzenesulfonic acid[23] as catalyst, a concentration of 10^{-3} M generally being sufficient.

In the case of alcohols, the reaction with acetic anhydride is also catalyzed, permitting their determination:

$$(CH_3CO)_2O + ROH \rightarrow CH_3COOR + CH_3COOH \tag{4}$$

The possible esterification of acetic acid with alcohols, or the hydrolysis of the esters formed above, takes place too slowly to cause interference.

Reagents: 2,4-Dinitrobenzenesulfonic acid, 0.1 M solution in dry acetonitrile. Prepare freshly every few weeks and keep at 0°C.

Acetic anhydride, 1 M solution in dry acetonitrile.

Water, 1 M solution in acetonitrile.

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[21] S. Marks and R. S. Morrell, *Analyst*, **56**, 428 (1931).

[22] G. Toennies and M. Elliott, *J. Am. Chem. Soc.*, **57**, 2136 (1935).

[23] J. N. Elgersma, *Rec. trav. chim.*, **48**, 770 (1929).

Sodium methylate, 0.1 M solution in methanol. Keep in a closed titration system for protection against carbon dioxide and evaporation. Standardize by comparison with a standard solution of sodium hydroxide, titrating each with hydrochloric acid to methyl red in the presence of equal concentrations of methanol[24] (*Cf.* p. 229).

Thymol blue indicator, 0.125% in methanol, treated with sufficient sodium methylate solution to neutralize the sulfonic acid group. Use 10 drops of indicator solution for every 20 ml. of solution being titrated.

Procedure for Water Determination: In general, enough acetic anhydride should be employed so that the initial content, allowing for the volume of the sample, will not exceed 0.04 M in tests which are to stand overnight, or 0.2 M in shorter tests. The quantity of sample taken should be such that after reaction the mixture will still be at least 0.01 M in acetic anhydride. Into each of several dry, glass-stoppered Erlenmeyer flasks one carefully measures the calculated amounts of acetic anhydride solution, previously mixed with enough of the catalyst (2,4-dinitrobenzenesulfonic acid solution) to make its concentration 0.002–0.004 M during the reaction. The total volume is brought to about 5 ml. with dry acetonitrile (see Note 5 below).

When one is determining water in acetonitrile, half of the above mixtures are regarded as blanks; to the others 5 ml. portions of the acetonitrile sample are added and all are allowed to stand for definite periods. For example, at the end of 3 hours a sample and a blank may be titrated with sodium methylate to a blue end-point with thymol blue. After longer periods, other pairs may be titrated to check the completeness of the reaction.

In analyzing nearly anhydrous ether, one uses a 50 ml. portion of the ether in each "blank" and a 100 ml. portion in each "sample." The titration difference therefore refers to a sample of 50 ml. This procedure serves to minimize differences in reaction rates and end-point recognition caused by the larger volumes of solution. Longer reaction times are required in such cases.

Procedure for Alcohol Determination: The procedure is much the same as for water determination. The essential difference is that after the alcohol has reacted with acetic anhydride, one decomposes the remaining anhydride with enough water (1 M solution in acetonitrile) to make the final water concentration from 0.01 to 0.1 M. Enough sodium methylate is then added to neutralize the dinitrobenzenesulfonic acid and stop catalytic action. At this point the solvent composition of the blank is made the same as that of the sample (by addition of as much sample as was used in the test) and both solutions are titrated.

Notes: (1) The method is intended primarily for the determination of small to moderate concentrations of water or alcohol, in solvents that are inert toward the reagents. It is not applicable to substances with acid or basic properties, or to those that decompose under the given conditions. Acetone interferes seriously if more than a trace is present, particularly in tests of longer duration.

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[24] *Cf.* T. F. Lavine and G. Toennies, *J. Biol. Chem.*, **101**, 727 (1933).

(2) As little as 0.001% of water can be detected in 50 ml. of ether. With 1% present the maximum error need not exceed 1% of the true value, according to Toennies and Elliott.

(3) Calculations are made in the same way as for the acetyl chloride-pyridine method, p. 210.

(4) In analyzing very dry samples the flasks used must first be dried for several hours at high vacuum, in the presence of an efficient desiccant.

(5) Care should be taken, through use of enough acetonitrile, to keep the catalyst from crystallizing. In ether, 5% of acetonitrile is sufficient for 0.004 M sulfonic acid, while in benzene, 10% is necessary.

(c) *Other Methods:* Lindner[25] makes use of the reaction between α-naphthyldichlorophosphine oxide and water for an acidimetric determination of the latter. Hydrochloric acid is evolved and titrated. An application of the method to the determination of oxygen in organic compounds is described by Lindner and Wirth.[26] By means of hydrogenation the oxygen is converted to water. Unfortunately, however, the water determination is very slow.

According to van Nieuwenberg,[27] cinnamoyl chloride has the advantages over naphthyldichlorophosphine oxide of being practically nonvolatile and reacting rapidly with water:

$$2C_3H_7COCl + H_2O \rightarrow (C_3H_7CO)_2O + 2HCl$$

The reagent, which may be prepared from cinnamic acid and thionyl chloride, melts at 36°C. and boils at 257.5° under standard pressure (100–110° at 1–2 mm.). It must be protected from exposure to the atmosphere. In the procedure, the sample and a moderate excess of molten reagent are placed in a small absorption flask and heated at 65° in a glycerol bath. The hydrogen chloride, carried over in a current of dry air, is caught in a small titration flask containing 2–4 ml. of water and is titrated with 0.02 N borax solution to a yellow color with methyl red.

The results obtained by van Nieuwenberg were high by from 0.02 to 0.09 mg. in tests with 1.5 to 8.0 mg. of water; he attributes the error to moisture in the air. Errors from this source should be preventable by refinements in the apparatus and manipulation.

Bell[28] recommends the use of α-naphthoxydichlorophosphine, which reacts more rapidly than Lindner's reagent though the determination still requires considerable elapsed time. Each millimole of hydrochloric acid liberated corresponds with one millimole of water:

$$C_{10}H_7OPCl_2 + 2H_2O \rightarrow C_{10}H_7OP(OH)_2 + 2HCl$$

Naphthoxydichlorophosphine is prepared from α-naphthol and phosphorus trichloride in an all-glass apparatus, according to the method of Kunz.[29]

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[25] J. Lindner, *Z. anal. Chem.*, **66**, 305 (1925).

[26] J. Lindner and W. Wirth, *Ber.*, **B70**, 1025 (1937).

[27] C. J. van Nieuwenberg, *Mikrochim. Acta*, **1**, 71 (1937).

[28] R. P. Bell, *J. Chem. Soc.*, **135**, 2903 (1932).

[29] P. Kunz, *Ber.*, **27**, 2560 (1894).

It is purified by distillation in vacuum and aeration (with dry air) at 100°C. The boiling point is 180° at 18 mm. pressure. In solid form the compound reacts slowly with water, but a solution in benzene reacts rapidly.

In the method, a solution of reagent in a suitable solvent such as dry bromobenzene is placed in a tube through which air (dried over phosphorus pentoxide) can be bubbled. The air stream goes through a glass joint into a U-tube containing water to absorb hydrochloric acid. Air is first passed through the reagent solution alone at a steady rate (50 to 100 ml. per minute) until the amount of acid liberated within a given period, say an hour, diminishes to a constant value which represents vaporization of reagent. Then the sample is introduced and the test is continued until a new constant value is reached. The latter rate is regarded as the blank and a correction for it is applied on the basis of the entire time during which air has passed through the sample. Acid liberated during each interval is titrated with 0.1 N alkali and the total quantity, corrected for the blank, is calculated as equivalent to the amount of water in the sample.

Using 0.025 to 0.062 g. of water weighed in directly, Bell obtained results agreeing within 0.1 to 0.3 mg. Hydroxyl and amino compounds interfere.

For a more rapid approximation, one may allow the test to run 8 hours and omit the blank correction.

Ross[30] worked out a process employing benzoic anhydride, which appears to be precise and widely applicable but rather time-consuming. The sample and reagent are heated for 12 hours in a Carius tube at 110–120°C. and the liberated benzoic acid is titrated. Any methyl benzoate that is formed is determined gravimetrically. The original paper should be consulted for details of the method, which can be used in the presence of alcohols, aldehydes, and acetals if appropriate corrections are applied.

Fischbeck and Eckert[31] determine small quantities of water by allowing them to react with anhydrous aluminum chloride in a stream of hydrogen at 450°C.:

$$2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl$$

Special apparatus is necessary; aluminum chloride is volatile and must be condensed, with suitable correction for the part that is carried over. The hydrochloric acid is caught in an excess of standard sodium carbonate solution which is titrated back. Errors of from −0.5 to −2% were observed in tests with 5 to 8 mg. of water. Organic oxygen compounds interfere.

5. Bromo-acidimetric Methods.—When bromine acts upon an organic substance in an oxidizing or substituting manner, an equivalent amount is reduced to hydrobromic acid. On this reaction are based several acidimetric determinations, in which the excess of bromine is removed after oxidation or substitution and the liberated acid is titrated. Rosenthaler[32] removes the bromine by blowing air through the solution; reduction with an excess of calomel, followed by filtration, is preferable in some respects. In all cases it is necessary to run blank tests, since bromine water invariably contains a little acid. Use of a freshly prepared bromine solution is to be recommended.

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[30] J. Ross, *J. Soc. Chem. Ind.*, **51**, 121T (1932).

[31] K. Fischbeck and E. Eckert, *Z. anal. Chem.*, **112**, 305 (1938).

[32] L. Rosenthaler, *Pharm. Acta Helv.*, **6**, 179, 209 (1931); *Chem. Abstracts*, **26**, 3333, 3453 (1932).

Determination of Phenol[32]*:* In the presence of excess bromine, ordinary phenol reacts to form difficultly soluble tribromophenol bromide and four equivalents of acid per mole:

$$C_6H_5OH + 4Br_2 \rightarrow C_6H_2Br_3OBr + 4HBr$$

Place a measured amount of the phenol solution in a 100 ml. volumetric flask, add an excess of bromine water, make to volume, and shake until the precipitate is coagulated. Pipette an aliquot portion of the filtered solution into a flask and bubble air through to remove bromine. Titrate this solution, and also a blank which has been carried through the same procedure, with 0.1 N alkali. Methyl red serves as indicator. Each milliliter of alkali represents 2.353 mg. of phenol.

Kolthoff[33] recommended a modification of the method: to 10 ml. of 0.1 M phenol add 40 ml. of freshly saturated bromine water. Shake for 5 or 10 minutes, then introduce an excess of calomel (about 2 g.) and shake until the bromine has been reduced. Filter, wash, and titrate with 0.1 N alkali to methyl red or bromocresol green. The precipitate must be removed before addition of methyl red, which would otherwise be adsorbed.

Notes: (1) The results average about 2% high even though a blank correction is applied. The error may be reduced to about 0.8%, if instead of using calomel one extracts the brominated phenol and excess bromine with carbon tetrachloride or chloroform.

(2) Salicylic acid reacts to form tribromophenol bromide and carbon dioxide and may be determined in the same way.

Hydroquinone: Rosenthaler[34] applied his phenol method to the determination of hydroquinone, which is oxidized to quinone:

$$C_6H_4(OH)_2 + Br_2 \rightarrow C_6H_4O_2 + 2HBr$$

Details of the procedure are essentially the same as those given previously· Each milliliter of 0.1 N alkali corresponds to 5.50 mg. of hydroquinone.

Other Substances: Thiosulfate, thiocyanate, and cyanide may be determined in similar fashion:[34]

$$Na_2S_2O_3 + 4Br_2 + 5H_2O \rightarrow Na_2SO_4 + H_2SO_4 + 8HBr$$
$$(1 \text{ ml. } 0.1 \text{ N} \equiv 2.482 \text{ mg. } Na_2S_2O_3 \cdot 5H_2O)$$
$$KCNS + 4Br_2 + 4H_2O \rightarrow KHSO_4 + 7HBr + BrCN$$
$$(1 \text{ ml. } 0.1 \text{ N} \equiv 1.213 \text{ mg. } KCNS)$$
$$HCN + Br_2 \rightarrow HBr + BrCN$$
$$(1 \text{ ml. } 0.1 \text{ N} \equiv 2.702 \text{ mg. } HCN)$$

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[33] I. M. Kolthoff, *Pharm. Weekblad*, **69, 1147 (1932).**

[34] L. Rosenthaler, *Pharm. Acta Helv.*, **7, 45 (1932).**

Hydrogen peroxide reacts more slowly and should be allowed to stand for 10 minutes before removal of bromine:[35]

$$H_2O_2 + Br_2 \rightarrow 2HBr + O_2$$
$$(1 \text{ ml. } 0.1 \text{ N} \equiv 1.70 \text{ mg. } H_2O_2)$$

To determine arsenous acid, one brominates and then titrates to thymol blue as indicator (change from yellow to blue) so that the end-point corresponds with formation of disodium arsenate:[35]

$$As_2O_3 + Br_2 + 2H_2O \rightarrow As_2O_5 + 4HBr$$
$$(1 \text{ ml. } 0.1 \text{ N} \equiv 2.474 \text{ mg. } As_2O_3)$$

In determining mercuric sulfide a bromine–potassium bromide solution is used.[35] To 20 ml. of water add 10 g. of potassium bromide and 2.5 ml. of bromine. Probably the removal of excess bromine from such a solution is a slow process, by simple aeration.

$$HgS + 4Br_2 + 2KBr + 4H_2O \rightarrow HgBr_2 + K_2SO_4 + 8HBr$$
$$(1 \text{ ml. } 0.1 \text{ N} \equiv 2.908 \text{ mg. } HgS)$$

6. Determination of Aldehydes.—(*a*) ***Ammonia Method:*** Formaldehyde unites with ammonia to form hexamethylenetetramine:

$$6HCHO + 4NH_3 \rightleftarrows C_6H_{12}N_4 + 6H_2O$$

Application of this reaction to the determination of ammonia has previously been described (p. 158). Legler[36] long ago used a converse procedure for the assay of formalin solutions. The method has been tested and altered by various authors.[37] Smith[38] effected an important improvement by working with ammonium chloride and sodium hydroxide rather than with ammonia.

The reaction between formaldehyde and ammonia does not take place instantaneously. Most workers hold that at least an hour should be allowed before titrating. According to the authors' experience this much time is sufficient.

The question of a suitable indicator appears to have offered more difficulty, so that conflicting opinions have been expressed in the literature, yet the problem is easily solved. Hexamethylenetetramine behaves as a very weak base ($K_b = 8 \times 10^{-10}$; $p_K = 9.1$);

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[35] L. Rosenthaler, *Pharm. Acta Helv.*, **7**, 88 (1932); *Chem. Abstracts*, **26**, 4556 (1932).

[36] L. Legler, *Ber.*, **16**, 1333 (1883).

[37] For a complete bibliography of the earlier literature, see F. Mach and R. Herrmann, *Z. anal. Chem.*, **62**, 129 (1923).

[38] C. E. Smith, *Am. J. Pharm.*, **70**, 86 (1898).

therefore the case resolves itself into the titration of one weak base, ammonia, in the presence of another that is still weaker. As was mentioned on p. 149, the titration exponent when the two bases have equal initial concentrations may be calculated:

$$p_T = 14 - \tfrac{1}{2}(p_{K_1} + p_{K_2}) = 14 - \tfrac{1}{2}\,(4.7 + 9.1) = 7.1$$

If ammonium salts are present in excess, as generally happens, the reaction at the end-point becomes slightly more acid. In practice a p_H of 6.7 gives good results. Phenol red, neutral red, and rosolic acid are suitable if the titrations are carried completely to the acid colors. Bromothymol blue can also serve, if the end-point is taken at a green color. Methyl orange is unsatisfactory since hexamethylenetetramine binds a little acid at p_H 4.0. Therefore one would find too much free ammonia in the back-titration and consequently would obtain too low results for formaldehyde.

Procedure: Prepare the sample so that about 3 g. of 37% formaldehyde is present in 25 ml. of neutral solution, in a glass-stoppered Erlenmeyer flask. Add 15 ml. of neutral 20% ammonium chloride solution, followed by 40 ml. of 1 N sodium hydroxide from a rapidly flowing burette. Stopper the flask and allow it to stand for an hour or two, then titrate with 1 N hydrochloric acid to the acid color of phenol red, neutral red, or rosolic acid, or to the green color of bromothymol blue. Each milliliter of 1 N alkali used up corresponds to 45.0 mg. of formaldehyde.

Notes: (1) The procedure is also suitable for a solution of one-tenth the above concentration. For the same volume one adds 0.3 g. of ammonium chloride; 0.1 N alkali and acid are used.

(2) Commercial formaldehyde occasionally contains a little free formic acid which first should be neutralized to the same indicator that is to be used in the titration. Methyl alcohol is also likely to be present but it has no effect on the result.

(3) Foschini and Talenti[39] suggest working with a standard ammonia solution in place of ammonium chloride and sodium hydroxide. They determine the excess by distilling it under reduced pressure into standard acid.

(4) Acetaldehyde also reacts with ammonia, although slowly, and thus would interfere if present. Castiglioni[40] has outlined conditions under which the interference from acetaldehyde is minimized. To the solution is added an excess of neutral 5% ammonium sulfate. After 15 minutes there are introduced 2–3 drops of rosolic acid indicator and a measured quantity of 0.5 N sodium hydroxide, enough to bring the indicator to a distinctly alkaline color. The excess of base is titrated with 0.5 N acid.

(*b*) ***Hydrogen Peroxide Method:*** In the presence of alkali, formaldehyde is oxidized to formic acid by hydrogen peroxide. According to Blank and Finkenbeiner[41] two reactions can occur:

[39] A Foschini and M. Talenti, *Z. anal. Chem.*, **118,** 94 (1939).

[40] A. Castiglioni, *Z. anal. Chem.*, **119,** 287 (1940).

[41] O. Blank and H. Finkenbeiner, *Ber.*, **31,** 2979 (1898); **32,** 2141 (1899).

$$HCOH + H_2O_2 + NaOH \rightarrow HCOONa + 2H_2O$$

$$2HCOH + H_2O_2 + 2NaOH \rightarrow 2HCOONa + 2H_2O + H_2$$

Since in either case one mole of alkali reacts with one mole of formaldehyde, for analytical purposes it matters not which reaction predominates. Each milliliter of normal alkali corresponds to 30 mg. of formaldehyde. However, the procedure given by Blank and Finkenbeiner carries with it several potential sources of error. Formaldehyde may be decomposed by alkali alone, with formation of methanol and sodium formate as in the Cannizzaro reaction. A thorough investigation by Schoorl[42] showed that the order in which the reagents are added is without influence, provided that the peroxide and alkali are introduced in rapid succession. It may also be concluded from the work of Mach and Herrmann[43] that under these conditions the autodecomposition of formaldehyde is negligible.

Varying views concerning the time necessary for oxidation are given in the literature.[43] Naturally the temperature has a decisive effect upon the time requirement. The following procedure, developed by Schoorl, involves heating upon a steam bath for 15 minutes; it gives good results.

Procedure: To 3 g. of 37% formaldehyde solution or its equivalent, in an alkali-resistant flask, add 50 ml. of 1 N sodium hydroxide and an equal volume of 3% hydrogen peroxide, previously neutralized to phenolphthalein. Fit the flask with a soda–lime tube and digest for 15 minutes on a steam bath, then cool and titrate with 1 N hydrochloric acid. Each milliliter of 1 N alkali which has been used up corresponds to 30.0 mg. of formaldehyde; therefore the number of milliliters used is equal to the percentage when the sample weight is exactly 3 g.

Notes: (1) The procedure is also applicable to more dilute solutions.

(2) If the formaldehyde is originally acid, it should be neutralized to phenolphthalein or a correction should be applied. Generally the acidity is very low.

(3) According to Mach and Herrmann[43] acetaldehyde exerts a strong inhibitory action if it amounts to more than 4% of the formaldehyde content. Acetone behaves similarly though with much less effect. Neither is likely to be encountered in commercial formaldehyde. If a mixture is to be analyzed, however, one must take into account two difficulties that may be caused by acetone: the first, already mentioned, giving low results, and the second, that acetone itself is oxidized to an acid so that a high result may be found.

(4) The same authors state that alkali-soluble polymers of formaldehyde are also oxidized and their sum is therefore included in the total.

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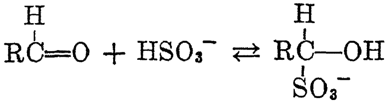
[42] N. Schoorl, *Pharm. Weekblad,* **43,** 1155 (1906).

[43] F. Mach and R. Herrmann, *Z. anal. Chem.,* **62,** 105 (1923).

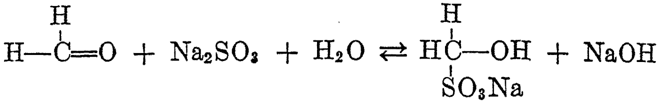
(*c*) ***Sulfite and Bisulfite Methods:*** Aldehydes react with bisulfite ions according to the equation:



$$R\overset{\overset{H}{|}}{C}{=}O + HSO_3^- \rightleftarrows R\underset{\underset{SO_3^-}{|}}{\overset{\overset{H}{|}}{C}}{-}OH$$

The equilibria in such reactions have been discussed in Volume I (p. 213). In the case of formaldehyde the addition product is formed practically quantitatively, at any reasonable dilution.

Sulfite Methods: Since sodium sulfite is hydrolyzed in aqueous solution, it reacts with formaldehyde:



$$H{-}\overset{\overset{H}{|}}{C}{=}O + Na_2SO_3 + H_2O \rightleftarrows H\underset{\underset{SO_3Na}{|}}{\overset{\overset{H}{|}}{C}}{-}OH + NaOH$$

The liberated alkali can be titrated to phenolphthalein without interference from the bisulfite addition compound, which reacts neutral to this indicator. Seyewetz[44] and Lemme[45] have made use of these facts in simple and rapid methods for formaldehyde determination. One difficulty arises in that sodium sulfite reacts appreciably alkaline toward phenolphthalein (p. 145). Auerbach[46] recognized this and remarked correctly that "in applying a correction, one overlooks that the alkaline reaction of sulfite solution depends upon conditions of equilibrium which vary with the concentration and also change during the titration itself." Still greater errors result from the use of rosolic acid, suggested by Doby[47] and several others. In principle the best indicator is thymolphthalein, to which sodium sulfite reacts practically neutral. It is employed in the method of Täufel and Wagner,[48] which in our experience gives excellent results.

Reagent: Dissolve 250 g. of crystallized sodium sulfite in water to make one liter. This solution may be slightly alkaline to thymolphthalein but generally the error may be compensated for by a very small correction as determined in a blank test. Because of its susceptibility toward air oxidation and carbon dioxide absorption, the solution should not be stored for long periods.

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[44] A. Seyewetz and co-workers, *Bull. soc. chim.*, **27**, 1212 (1902); **31**, 691 (1904).

[45] G. Lemme, *Chem.-Ztg.*, **27**, 896 (1903).

[46] F. Auerbach and co-workers, *Arb. kaiserl. Gesundh.*, **22**, 588 (1905); **47**, 116 (1914).

[47] G. Doby, *Z. angew. Chem.*, **20**, 353 (1907).

[48] K. Täufel and C. Wagner, *Z. anal. Chem.*, **68**, 25 (1926).

Procedure: Weigh out a 3 g. sample of 37% formaldehyde or an equivalent quantity of a more dilute solution and neutralize to thymolphthalein (3 drops of 0.1%). Add 50 ml. of sulfite reagent and titrate with 1 N hydrochloric acid until completely colorless. To be sure that sufficient sulfite is present, add a little more at the end and continue the titration if the color returns.

More dilute solutions can also be titrated well. With less than 0.1 g of pure formaldehyde present in 25 ml. of neutral solution, one adds 10 ml. of sulfite reagent and titrates slowly with 0.1 N acid until the color fades and does not return within 3 minutes.

Notes: (1) With rapid titration the blue color may disappear before the true end-point is reached. Only a little bisulfite ion is present in strongly alkaline solution and the formaldehyde is not converted entirely to the addition product. During titration the equilibrium shifts favorably but toward the end, when not much aldehyde remains, the reaction becomes slow; one should therefore allow several minutes before considering that the titration is finished.

(2) Acetaldehyde and acetone interfere since they are partially titrated under these conditions. According to the studies of Kerp[49] the addition of acetaldehyde to bisulfite takes place more rapidly than that of acetone. Moreover, the complex dissociation constant is greater in the case of the acetone compound, so that acetone reacts very incompletely. Methanol has practically no detrimental effect.

(3) In the determination of other aldehydes or of ketones, the incompleteness of the reaction with sulfite in alkaline solution must be considered. The smaller the reaction velocity and the larger the complex dissociation constant, the poorer are the results (*cf.* Vol. I, p. 215).

Bisulfite Methods: Determinations of aldehydes with bisulfite have been outlined repeatedly in the literature. Kleber[50] treated formaldehyde with an excess of sodium bisulfite solution previously standardized with alkali to phenolphthalein, and titrated the excess to the same indicator. Others have used rosolic acid. What has been said about indicators for the sulfite method holds as well here; thymolphthalein is the most satisfactory.

Procedure: To 25 ml. of about 0.1 M formaldehyde solution, neutralized to thymolphthalein, one adds at least 30 ml. of 0.1 M sodium bisulfite and allows to stand for 15 minutes, then titrates the excess bisulfite with standard alkali. The bisulfite solution is standardized in a blank titration.

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[49] W. Kerp, *Arb. kaiserl. Gesundh.*, **21**, 180 (1904). W. Kerp and E. Baur, *ibid.*, **26**, 231 (1907). See also Vol. I, pp. 213–222.

[50] C. Kleber, *Pharm. Rev.*, **22**, 94 (1904), through *Chem. Zentr.*, **1904**, I, 1108, and *Z. anal. Chem.*, **44**, 442 (1905).

Notes: (1) Good results can also be obtained with stronger solutions; however, for the assay of formalin the direct determination with sulfite is more practical.

(2) In the determination of other aldehydes or ketones, the considerations of Note 3 under the sulfite method are also applicable here.

(d) Hydroxylamine Methods: Condensation reactions involving aldehydes or ketones and salts of hydroxylamine have been known for a long time and proposed for acidimetric determination of carbonyl compounds,[51] but have not met with much favor until recently.

Hoepner[52] used the method for acetone determination:

$$(CH_3)_2CO + H_2NOH \cdot HCl \rightleftarrows (CH_3)_2{=}NOH + H_2O + HCl$$

but Marasco[53] found an error of -5.5% in the results. The same error was obtained in formaldehyde determinations, though with an empirical correction the method could be made useful. Neuberg and Gottschalk[54] noted even lower results when dilute solutions were employed.

According to A. H. Bennett and Donovan[55] the reaction rates of hydroxylamine hydrochloride and various aldehydes are slow, so that sufficient time must be allowed. They considered their modified procedure satisfactory for a number of natural aldehydes, but not for camphor. C. T. Bennett and co-workers[56] independently used a somewhat similar titration for the aldehydes of citronella and lemon oils. The procedures were not found entirely suitable by Bryant and Smith,[57] who described a modification in which pyridine serves to buffer the solution and thereby increases the rate of reaction. Alcohol also appears to have a beneficial effect and is called for in most of the proposed procedures.

Method of Bryant and Smith.

Reagents: Alcoholic sodium hydroxide (0.5 N in 90% methanol)—standardize at the temperature at which it is to be used, against a known quantity of standard aqueous acid. Hydroxylamine hydrochloride (0.5 N in 80% ethanol)—dissolve 35 g. of a reasonably pure salt in 160 ml. of distilled water and dilute to a liter with 95% ethanol. Pyridine–indicator mixture—to 20 ml. of C.P. pyridine add 10 ml. of 0.1% bromophenol blue (alcoholic) and dilute to a liter with 95% ethanol.

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[51] A. Brochet and R. Cambrier, *Compt. rend.*, **120**, 449, 557 (1895).

[52] K. Hoepner, *Z. Untersuch. Nahr. u. Genussm.*, **34**, 453 (1917).

[53] M. Marasco, *Ind. Eng. Chem.*, **18**, 701 (1926). According to C. O. Haughton, *Ind. Eng. Chem., Anal. Ed.*, **9**, 167 (1937), Marasco's results indicate nearly twice as great an error as that which actually occurs.

[54] C. Neuberg and A. Gottschalk, *Biochem. Z.*, **146**, 175 (1924).

[55] A. H. Bennett and F. K. Donovan, *Analyst*, **47**, 146 (1922).

[56] C. T. Bennett and M. S. Salamon, *Analyst*, **52**, 693 (1927). C. T. Bennett and T. T. Cocking, *ibid.*, **56**, 79 (1931).

[57] W. M. D. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **57**, 57 (1935).

Procedure: Into clean 300 ml. "citrate" pressure bottles measure 30 ml. portions of hydroxylamine hydrochloride reagent and 100 ml. portions of pyridine–indicator mixture. Reserve at least one bottle as a blank and into the others place the weighed or measured samples, in such proportions that more than one-third, preferably one-half, of the reagent in each bottle will remain after the reaction. Cap the bottles and allow to stand at room temperature or in a steam bath at 98–100°C. for a length of time suited to the particular material (see Table). Allow heated samples to cool spontaneously to within 5° of room temperature. Titrate the contents of each sample bottle with 0.5 N alcoholic alkali until the color matches that of the

CONDITIONS FOR DETERMINATION OF ALDEHYDES AND KETONES (ACCORDING TO BRYANT AND SMITH[57])

Substance	Time Required, Room Temperature	Time Required, 98–100°C.
Propionaldehyde		2 hours
Acetone	10 minutes	
Isobutyraldehyde	10 minutes	
2- or 3-Pentanone	30 minutes	
2-Hexanone	30 minutes	
2-Methyl-3- or -4-pentanone		2 hours
2,2-Dimethyl-3-butanone		1 hour
2,4-Dimethyl-3-pentanone	48 hours	2 hours, plus 18 hours cold after heating
2-Methyl-(3)-hexen-5-one		30 minutes
2,4-Dimethyl-3-hexanone	17 hours	
2-Octanone	30 minutes	
dl-Camphor		5 hours (0.5 g. sample)
Furfural	30 minutes	
Benzaldehyde	30 minutes	
p-Tolualdehyde	30 minutes	
Dimethylbenzaldehyde	30 minutes	
Cinnamaldehyde		2 hours
Acetophenone		2 hours
Salicylaldehyde		1 hour
o-Nitrobenzaldehyde	30 minutes	
p-Chlorobenzaldehyde	10 minutes	
Benzophenone		3 hours
Benzoin	>14 hours	<1 hour
Benzil (first step)	14 hours	<1 hour
4-Heptanone	30 minutes	
2-Ethyl-1-hexanal	30 minutes	
Glucose		2 hours
Carvone	24 hours	2 hours

blank (greenish blue). Avoid violent agitation of the mixture, which may cause precipitation of salt.

Each millimole of alkali required corresponds with one millimole of carbonyl radical (aldehyde or ketone).

Notes: (1) Acid or basic substances in the samples naturally interfere. Presumably corrections might be applied to compensate for their effects. Inert organic solvents are not objectionable except in such quantities as would affect the indicator color or retard the reaction unduly. Compounds of ferric iron and possibly of other oxidizing elements may cause decomposition of the reagent and lead to high results. In some cases these may be removed by preliminary distillation.

(2) With samples of optimum size, the results are usually reproducible to within less than 1%. The absolute accuracy is uncertain since in many cases the compounds used for testing the method were not of known purity.

Method of Schultes: The use of hydroxylammonium sulfate instead of the chloride, and of bromophenol blue as indicator, has been recommended by Schultes.[58] The hydroxylammonium sulfate is used in the form of an 0.5 N aqueous solution, neutralized to bromophenol blue; a volume of this solution approximately equal to the expected titration volume is added to the neutral sample. From 3 to 5 drops of indicator solution (0.1% in 30% ethanol) are added, the mixture is shaken very briefly, and then is titrated at once with 0.1 N sodium hydroxide. In some cases, as with benzophenone, heating may be necessary.

Notes: (1) Schultes reported results accurate to within 1% on benzaldehyde, acetaldehyde, butyraldehyde, acetophenone, and benzophenone. He attributes his success with the method to the use of bromophenol blue indicator, since when using methyl orange he obtained results about 4% low on butyraldehyde.

(2) For the assay of benzaldehyde, Schubert and Dinkelspiel[59] prefer tetrabromophenol blue as indicator. They also recommend hydroxylammonium sulfate as reagent, but in 50% methanol solution. For details of their procedure, which is capable of giving excellent results, the original paper should be consulted.

(3) Krajcinovic[60] reported good results for acetone using hydroxylamine hydrochloride as reagent and methyl red as indicator. The reagent (1–2 g.) is dissolved in a little water, in a 200 ml. Erlenmeyer flask, and is neutralized to methyl red. The sample is added and the mixture is titrated with 0.1 N alkali. Krajcinovic regarded the procedure as superior to Messinger's iodometric method (Vol. III), for samples that contain ethanol or ethyl acetate.

(4) Camphor and hexetone cannot be determined directly by Schultes' method. Schulek and Wolstadt[61] have described a more elaborate procedure in which one refluxes the mixture for 4 hours in alcoholic medium, neutralizes and titrates the unused hydroxylamine hydrochloride to phenolphthalein.

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[58] H. Schultes, *Z. angew. Chem.*, **47**, 258 (1934).

[59] M. Schubert and J. G. Dinkelspiel, *Ind. Eng. Chem., Anal. Ed.*, **14**, 154 (1942).

[60] M. Krajcinovic, *Chem.-Ztg.*, **55**, 894 (1931). See also C. O. Haughton, *Ind. Eng. Chem., Anal. Ed.*, **9**, 167 (1937).

[61] E. Schulek and R. Wolstadt, *Z. anal. Chem.*, **104**, 183 (1936); *Chem. Abstracts*, **30**, 3586 (1936).

(5) Small quantities of formaldehyde, benzaldehyde, or other simple aldehydes in methanol-soluble compounds such as monomeric styrene may be determined with considerable sensitivity by mixing 10 g. of sample with 10 ml. of methanol, adding 0.2 ml. of 0.04% thymol blue in 50% ethanol, neutralizing just to the yellow color and introducing 10 ml. of freshly prepared and neutralized 2% hydroxylamine hydrochloride in methanol. If aldehyde is present the mixture becomes pink quickly. After one hour, and again after two hours, it is titrated with 0.1 N aqueous sodium hydroxide to the yellow color. The sum of the two titrations is used in calculating the result. If the second titration exceeds 0.5 ml., a third one should be made after another hour. With only about 0.03% formaldehyde or 0.1% benzaldehyde present the result is likely to be 12–15% low, so that an empirical correction (determined by the analysis of a known mixture) should be applied.

(*e*) ***Dimedon Method for Aldehydes:*** Vorländer and co-workers[62] found that 5,5-dimethylcyclohexane-1,3-dione ($C_8H_{12}O_2$, dimedon or methon) reacts with aldehydes but not with ketones. One mole of aldehyde binds two moles of reagent, splitting out a mole of water. The product may be regarded as a derivative of either a diphenyl- or a triphenylmethane, depending upon whether the aldehyde is aliphatic or aromatic:

$$HCHO + 2C_8H_{12}O_2 \rightarrow CH_2(C_8H_{11}O_2)_2 + H_2O$$
$$C_6H_5CHO + 2C_8H_{12}O_2 \rightarrow C_6H_5CH(C_8H_{11}O_2)_2 + H_2O$$

Since the products have the character of enol acids they may be titrated to phenolphthalein. Formaldehyde yields a monobasic acid, acetaldehyde a dibasic. The products are difficultly soluble and both gravimetric and acidimetric methods have been described. According to Yoe and Reid[63] the solution should be buffered at a p_H of 4.6 in order for quantitative precipitation to take place.

Reagent: Dimedon of melting point 148–150°C. is commercially available. A saturated aqueous solution contains 0.41 g. per 100 ml. at 25°, 1.19 g. at 50°, 3.02 g. at 80°, and 3.84 g. at 90°. The solution decomposes slowly either in the dark or exposed to light. For aldehyde determinations, one dissolves 20 g. of dimedon in 250 ml. of alcohol and dilutes to 500 ml. with water. This solution should react weakly acid, since the reagent itself behaves as a monobasic acid.

Procedure for Formaldehyde or Acetaldehyde: To the aldehyde sample one adds an excess of dimedon solution and keeps the mixture for 12 hours at 50°C., followed by 12–16 hours at room temperature. Then the precipitate is filtered off, washed with water, and dissolved in alcohol. The solution is titrated with standard alkali to phenolphthalein; in the case of acetaldehyde the titration is carried out at 65–70°. Each milliliter of 0.1 N sodium hydroxide corresponds to 3 mg. of formaldehyde or 2.2 mg. of acetaldehyde. One can add, as a mean correction for solubility loss, 0.1 mg. of formaldehyde or 1.1 mg. of acetaldehyde per 100 ml. of aqueous solution or wash water (at room temperature).

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[62] D. Vorländer, *Z. anal. Chem.*, **77**, 241, 321 (1929).

[63] J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

Notes: (1) Unfortunately the procedure is not described with sufficient detail in Vorländer's papers. Further investigation is desirable.

(2) Dilute hydrochloric or sulfuric acid prevents complete precipitation and any free acid should therefore be neutralized. Larger amounts of alcohol interfere in the same way, though small quantities of alcohol or of acetone are said to cause scarcely any difficulty.

7. Determination of Various Organic Substances.—(*a*) ***Chloral Hydrate:*** Chloral hydrate reacts with alkali to yield chloroform and a salt of formic acid:

$$CCl_3CH(OH)_2 + NaOH \rightarrow CHCl_3 + HCOONa + H_2O$$

The reaction was applied by Meyer and Haffter[64] in an assay method. It does not take place instantaneously; one must add an excess of alkali and titrate back after some time has elapsed. This introduces the possibilities that some chloroform may hydrolyze and that other side reactions may also occur. Belohoubek[65] noted the formation of carbon monoxide in certain cases and this was confirmed by Rosenthaler and Reis.[66] While some authors[67] have said that the alkalimetric determination of chloral hydrate gives good results, others have pointed out that the time, temperature, and excess of alkali should be controlled in order to minimize interfering reactions.[68] By working at room temperature and with 0.1 N solutions one encounters little difficulty. Kolthoff[69] was able to obtain results accurate to within 1% or better, by the method given below.

Procedure: To 25 ml. of about 0.1 M chloral hydrate solution in a glass-stoppered flask add 30 ml. of 0.1 N sodium hydroxide and let stand for 15 minutes, stoppered. Titrate the excess alkali with 0.1 N hydrochloric acid, to phenolphthalein. One ml. of 0.1 N alkali corresponds to 16.54 mg. of chloral hydrate.

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[64] V. Meyer and H. Haffter, *Ber.*, **6**, 600 (1873).

[65] A. Belohoubek, *Chem. Zentr.*, **1898, I,** 558, 663.

[66] L. Rosenthaler and R. Reis, *Apoth.-Ztg.*, **22,** 678 (1907), through *Chem. Zentr.*, **1907, II,** 891.

[67] T. E. Wallis, *Pharm. J.*, **22,** 162 (1906). C. van Rossem, *Z. physik. Chem.*, **62,** 699 (1908).

[68] C. G. Hinrichs, *Pharm. J.*, **16,** 530 (1903). P. A. W. Self, *ibid.*, **25,** 4 (1907). J. Garnier, *Bull. sci. pharmacol.*, **15,** 77 (1908), through *Chem. Zentr.*, **1908, I,** 1492.

[69] I. M. Kolthoff, *Pharm. Weekblad*, **60,** 2 (1923).

(*b*) ***Salts of Organic Acids:*** There are several general methods of approach to the problem of determining organic acid salts:

1. The displacement titration of a strong base bound to a weak acid has been discussed in Chapter V. Good results are obtainable with most salts of this type if 1 N solutions can be employed. Certain acids are weak enough to permit the use of more dilute solutions in the titration (p. 150).

2. The salt may be ignited to sodium carbonate which in turn may be titrated for total alkalinity. Formation of a little sodium oxide is not harmful. Hydrated salts are first dried and then charred carefully in a platinum crucible. The heating is preferably done in an electric furnace but a burner flame may be used if one provides protection from sulfur-bearing gases. When smoking ceases, the temperature is raised for a period, with the crucible only half covered, until the carbon is oxidized. Later the residue is cooled, dissolved in water, and titrated with acid to methyl yellow.

Occasionally the ignited product may still contain some carbon, which should be removed with the aid of an ashless filter and burned down again. This second residue is extracted and the solution combined with the first filtrate. Otherwise some alkali may be lost through adsorption on the carbon.

If the salt contains free alkali (sodium hydroxide or carbonate), high results are obtained. In some cases a correction may be determined by titrating the free alkali of a separate sample, to thymolphthalein or phenolphthalein. The considerations of Chapters IV and V should be taken into account in this connection.

The method is not applicable to salts of organic acids which contain halogens, sulfur, phosphorus, or arsenic.

3. Many organic acids are soluble in ether. Salts of these may be dissolved in water, treated with a slight excess of sulfuric acid, and extracted with ether until no more organic acid remains in the aqueous phase. The ether is vaporized (spontaneously at room temperature if the acid is volatile) and the residue is titrated with standard alkali. If the acid is not easily soluble in water, it may be dissolved in methanol, ethanol, or an alcohol-acetone mixture and titrated with alcoholic alkali. Bromothymol blue is a suitable indicator for the titration of many moderately weak organic acids (aqueous K_a down to 10^{-7}) in alcohol.

In many cases it is preferable to make the extraction with a solvent such as methylene chloride or carbon tetrachloride, which is more dense than water. When not too much solvent is required, the evaporation may be omitted and the extract may be mixed directly with alcohol and titrated with alcoholic alkali as indicated above.

4. Very volatile acids may be distilled and titrated in the distillate. Thus one liberates the acetic acid from an acetate by acidifying with sulfuric or phosphoric acid and distilling. The solution should be brought to a small

volume, then either diluted with water and distilled again or else distilled with the aid of steam. To drive over the last trace of acetic acid is difficult.

Salts of acids which are only slightly volatile or slightly soluble in water, such as the more highly chlorinated phenols, may be analyzed by prolonged steam distillation of an acidified solution, extraction of the acid from the distillate (as in 3 above), and titration of the extract. One should make sure that all of the acid is recovered from the condenser. Methods of this type are of importance in the analysis of materials containing phenolic fungicides, germicides, etc.

In addition, more or less specific methods can be developed for certain salts. For example, Fuchs[70] determines neutral alkali formates by titration of the hydrochloric acid liberated during oxidation with mercuric chloride:

$$HCOONa + 2HgCl_2 \rightarrow NaCl + Hg_2Cl_2 + HCl + CO_2$$

Instead of using an indicator, Fuchs titrates with alkali to the appearance of a yellow precipitate of mercuric oxide. Oldeman[71] recommends the more elegant method of adding sodium chloride (to tie up the excess mercuric chloride) and titrating to phenolphthalein.

Procedure: The neutral salt, or mixture of acids carefully neutralized to phenolphthalein, is transferred to a 100 ml. volumetric flask. Some pure sodium acetate (formate-free) should be added if not much was originally present, then a liberal excess of saturated mercuric chloride should be introduced, plus enough water to make the volume about 75 ml. The mixture is heated gently until carbon dioxide begins to be evolved. After the main reaction is over, heating is continued for 15 minutes at just below boiling, on the steam bath or with a very small flame. Meanwhile the flask should be shaken carefully at intervals. Next the contents are cooled, made up to the mark, mixed, and filtered. To a 50 ml. aliquot portion of the filtrate is added an excess of sodium chloride and the free acid is titrated with standard alkali to phenolphthalein. 1 ml. of 0.1 N alkali is equivalent to 4.6 mg. of formic acid.

(c) ***Acid Anhydrides:*** Smith and Bryant[72] found that a solution of an acid anhydride in pyridine may be titrated with aqueous alkali, the hydrolysis taking place very rapidly:

$$(RCO)_2O + 2NaOH \rightarrow 2RCOONa + H_2O \qquad (1)$$

Naturally any free acids present would be titrated at the same time. If a methanol solution of an identical sample is titrated with standard sodium methylate solution, free acids are again neutralized but the anhydride contributes only half as much acidity as in reaction (1):

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[70] P. Fuchs, *Z. anal. Chem.*, **78**, 125 (1929).

[71] R. G. C. Oldeman, *Pharm. Weekblad*, **68**, 379 (1931).

[72] D. M. Smith and W. M. D. Bryant, *J. Am. Chem. Soc.*, **58**, 2452 (1936).

$$(RCO)_2O + CH_3ONa \rightarrow RCOOCH_3 + RCOONa \qquad (2)$$

Therefore the difference between (1) and (2) is a direct measure of the amount of anhydride initially present.

Procedure: (1) Weigh out from 1 to 3 g. of acid anhydride, mix with 25 ml. of pure pyridine, and titrate with 0.5 N aqueous sodium hydroxide to phenolphthalein or thymol blue. (The indicator should be made up in dry dioxane or acetone rather than alcohol, which might cause ester formation.)

(2) Place a duplicate sample in a dry 250 ml. glass-stoppered volumetric flask and dissolve, if the material is a solid, in 20 to 30 ml. of anhydrous methanol or acetone. Warm if necessary to effect solution of the sample. Titrate directly with 0.5 N sodium methylate in methanol, to the same indicator used in (1). The excess of reagent required in (1) over that taken in (2) is proportional to the anhydride content; each milliliter of 0.5 N solution is equivalent, for example, to 51.05 mg. of acetic anhydride.

Notes: (1) The sodium methylate reagent is prepared by dissolving 11.5 g. of metallic sodium in a liter of dry C.P. methanol. This solution and the aqueous alkali should be compared frequently against standard 0.5 N acid.

(2) Unreactive compounds such as camphoric anhydride may be heated with the alkalies and then cooled before the back-titrations are made. Esters would interfere in this case, but generally do not interfere when the reactions are carried out at room temperature. Alkyl formates, however, and unstable lactones such as glucono-δ-lactone, are hydrolyzed in aqueous solution and thus cause erroneous results.

(d) Acid Amides: It has been found by Mitchell and Ashby[73] that unsubstituted amides in the presence of pyridine react quantitatively with 3,5-dinitrobenzoyl chloride:

$$RCONH_2 + (NO_2)_2C_6H_3COCl \rightarrow RCN + (NO_2)_2C_6H_3COOH + HCl \qquad (1)$$

The excess of reagent is acylated with methanol:

$$CH_3OH + (NO_2)_2C_6H_3COCl \rightarrow (NO_2)_2C_6H_3COOCH_3 + HCl \qquad (2)$$

With the aid of these reactions it was possible for Mitchell and Ashby to develop a useful procedure for the determination of various unsubstituted amides of carboxylic acids. The increase in acidity of

[73] J. Mitchell, Jr., and C. E. Ashby, *J. Am. Chem. Soc.*, **67**, 161 (1945).

the sample as compared with a blank is equivalent to the quantity of amide taken.

Reagent: To prepare an approximately 2 M solution of 3,5-dinitrobenzoyl chloride, dissolve 461 g. of the Eastman product in sufficient pure, anhydrous 1,4-dioxane to make one liter of solution. Colored impurities may be removed by treatment with activated charcoal, followed by a quick filtration. Care should be taken to minimize exposure to moisture.

Procedure: Weigh out a sample containing about ten milliequivalents of amide and place in a 250 ml. glass-stoppered volumetric flask containing 5 ml. of pyridine and 15 ml. of reagent. The reagent should be accurately measured and a duplicate portion together with pyridine alone should be carried along as a blank. Place each on a water bath at 60°C. for 30 minutes (see Note 1 below), then cool in an ice bath. Add 2 ml. of dry methanol, let stand for 5 minutes and add 25 ml. more. Titrate with 0.5 N sodium methylate in methanol (p. 229) using phenolphthalein or ethyl bis-(2,4-dinitrophenyl) acetate as indicator.

A correction should be applied for any free acid or water in the sample. Aside from this, each milliequivalent of sodium methylate taken for the sample, above that required for the blank, corresponds to one millimole of $—CONH_2$.

Notes: (1) Amides of dibasic acids are less soluble and should be ground to a fine state before the analysis. Heating should be prolonged to an hour, at a temperature of 70°C., and the flask should be shaken frequently. Addition of a few glass beads is helpful.

(2) High results are obtained with malonamide, urea, biuret, and acetyl urea, which yield interfering acid substances. Formamide gives colored products so that a potentiometric titration is required; it also yields a weak acid which does not interfere if some formaldehyde is added. Oxamide reacts only partially and allyl urea not at all.

(3) Aldoximes interfere, presumably giving the same reaction products as the corresponding amides. Alcohols and amines consume the reagent but otherwise do not interfere.

Urea: Taylor[74] has made use of the enzymatic hydrolysis of urea in its direct determination. Urea and urease, together with a small excess of standard hydrochloric acid, are allowed to react for several hours in an autoclave under 2 to 4 atmospheres pressure. After cooling, the excess acid is titrated with alkali to methyl orange. Although the method is capable of excellent accuracy, it is rarely employed since for most purposes the distillation method (p. 176) is more convenient.

(*e*) ***Ethylene Oxide:*** According to Deckert,[75] ethylene oxide in a sodium chloride solution containing hydrochloric acid reacts in the following way:

$$C_2H_4O + NaCl + H_2O \rightleftarrows CH_2OHCH_2Cl + NaOH$$

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[74] M. Taylor, *J. Am. Chem. Soc.*, **50**, 3261 (1928).

[75] W. Deckert, *Z. anal. Chem.*, **82**, 297 (1930).

This reversible reaction proceeds quantitatively to the formation of ethylene chlorohydrin only in the presence of acid. Lubatti[76] obtained low results by Deckert's method. He established that the ethylene oxide reacts directly with hydrochloric acid:

$$C_2H_4O + HCl \rightleftarrows CH_2OHCH_2Cl$$

and that this reaction is quantitative if the acid solution contains at least 30 g. of chloride or 43 g. of bromide per 100 ml. These high salt concentrations are essential.

Reagent: 0.10 N sulfuric acid, made up either in saturated magnesium chloride solution or in a solution containing from 49 to 53 g. of magnesium bromide per 100 ml. According to Kerckow,[77] one may also use a 1 N hydrochloric acid solution made up by dissolving 1205 g. of crystallized calcium chloride in 200 ml. of warm water, adding 110 ml. of 10 N hydrochloric acid and allowing to cool in the stock bottle. Some calcium chloride crystallizes at room temperature.

Procedure: The ethylene oxide sample, either measured as a gas or weighed as a liquid in a sealed bulb, is placed in a reaction flask (see Lubatti's original article for details) and treated with an excess of reagent, precisely measured. After the constituents have been mixed thoroughly, the excess acid is titrated with standard alkali to methyl orange. The difference between this titration and a blank on the same volume of reagent is equivalent to the quantity of ethylene oxide present.

(*f*) ***Mercaptans:*** In benzene solution, mercaptans (thio alcohols) react readily with aqueous mercuric chloride:

$$RSH + HgCl_2 \rightarrow RSHgCl + HCl$$

Sampey and Reid[78] made use of the reaction for the determination of mercaptans in benzene or naphtha solution.

Procedure: Dissolve about 0.7 millimole of mercaptan in 50 ml. of benzene and shake vigorously for about 3 minutes with 25 ml. of 1% mercuric chloride in water. The mercury salt which forms may or may not be soluble, depending upon what mercaptan is present. If no precipitate, or only a very little, is formed, separate the two layers and wash the benzene three times with 25 ml. portions of water. Titrate the combined aqueous layer and washings with 0.025 N sodium hydroxide, to methyl orange or methyl red. If a heavy precipitate is formed, titrate the mixture directly, very slowly and with frequent shaking. Only methyl orange can be used in this case.

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[76] O. F. Lubatti, *J. Soc. Chem. Ind.*, **51**, 361T (1932); **54**, 424T (1935).

[77] F. W. Kerckow, *Z. anal. Chem.*, **108**, 249 (1937).

[78] J. R. Sampey and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 3404 (1932).

Notes: (1) The recommended indicators show their color change a little too soon, which is necessary in order to prevent the precipitation of a basic mercury salt. To lessen the error, one should standardize the alkali against approximately as much hydrochloric acid as is liberated in the determination, and with the same indicator. (*Au. note:* Possibly bromothymol blue or phenol red might be used if a little sodium chloride were added to repress the acid reaction of mercuric chloride.)

(2) Unsaturated hydrocarbons interfere, causing high results.

(*g*) ***Alkyl Sulfides:*** Patein[79] observed that the bromine addition product of methyl sulfide is readily hydrolyzed to methyl sulfoxide, with liberation of hydrobromic acid:

$$(CH_3)_2SBr_2 + H_2O \rightarrow (CH_3)_2SO + 2HBr$$

The reaction has been applied to the determination of various alkyl sulfides by Sampey, Slagle, and Reid,[80] who worked out conditions under which the bromine addition compound is formed quantitatively.

Procedure: To 50 ml. of a dilute benzene solution of the sulfide in a 250 ml. glass-stoppered Erlenmeyer flask add 50 ml. of distilled water. Introduce saturated bromine water drop by drop, with shaking, until the color of bromine persists. Not more than 2 drops should be added in excess and this should be removed within 15 seconds by addition of a little saturated potassium iodide solution. The liberated iodine is reduced with sodium thiosulfate.

Separate the layers and extract all hydrobromic acid from the benzene by washing three times with 20 ml. portions of water. Titrate the combined aqueous layer and washings with 0.05 N alkali. Run a blank on the same amounts of water, benzene, and bromine water, reduced and extracted in the same way, and subtract from the sample titration to compensate for free acid in the bromine water.

Note: Interference is caused by the presence of any unsaturated hydrocarbon whose bromine addition product hydrolyzes readily, and presumably also by such substances as acetone and phenols.

(*h*) ***Nicotine:*** Small amounts of nicotine may, according to Nagy and Dickmann,[81] be precipitated with silicotungstic acid. The precipitate may be dissolved in an excess of alkali:

$$H_8Si(W_2O_7)_6 \cdot 2C_{10}H_{14}N_2 + 8NaOH \rightarrow Na_8Si(W_2O_7)_6 + 2C_{10}H_{14}N_2 + 8H_2O$$

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[79] G. Patein, *Bull. soc. chim.*, **50**, 203 (1888).

[80] J. R. Sampey, K. H. Slagle, and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 3401 (1932).

[81] L. Nagy and A. Dickmann, *Z. anal. Chem.*, **94**, 12 (1933).

and the latter back-titrated with hydrochloric acid. In titrating to methyl red the nicotine behaves as a monoacid base so that one mole of nicotine corresponds finally to three equivalents of alkali.

Procedure: Place several milliliters of the nicotine solution in a centrifuge tube, acidify with a few drops of 4 N sulfuric acid and precipitate the nicotine with 0.5 ml. of 10% silicotungstic acid. Allow to stand overnight, centrifuge well and draw off the clear liquid carefully with a small suction tube or filter stick. Wash with 2–3 ml. of water, centrifuge again, and draw off the water, repeating this process several times until the washings become neutral to litmus paper. From a microburette add a measured volume of 0.01 N alkali, sufficient to dissolve the precipitate, and titrate the excess back with 0.01 N hydrochloric acid to methyl red. Each milliliter of alkali consumed is equivalent to 0.54 mg. of nicotine.

(*i*) ***Theobromine:*** This substance is too weak an acid to be titrated directly with sodium hydroxide. Upon treatment with silver nitrate the sparingly soluble silver salt precipitates and an equivalent amount of nitric acid is liberated:[82]

$$C_7H_8N_4O_2 + Ag^+ \rightarrow AgC_7H_7N_4O_2 + H^+$$

Procedure: Weigh out a sample containing about 0.2 g. of theobromine, dissolve in 15 ml. of 0.1 N sulfuric acid and 100 ml. of water, boil out carbon dioxide, cool, and neutralize with alkali to phenol red. Add an excess of 0.1 N silver nitrate and titrate the liberated acid immediately with 0.05 or 0.1 N sodium hydroxide. 1 ml. of 0.1 N alkali corresponds to 18.0 mg. of theobromine.

Theophylline gives the same reaction.

(*j*) ***Acetylsalicylic Acid (Aspirin):*** Aspirin behaves both as an acid and as an ester. One determines the carboxyl group first, then hydrolyzes in an excess of alkali.

Procedure: Dissolve about 0.4 g. of aspirin in a few milliliters of alcohol and titrate the free acidity with 0.1 N sodium hydroxide to phenolphthalein. Add 30 ml. more of the alkali, or enough to provide a definite excess, boil for five minutes, cool under protection of a soda–lime tube, and titrate back with 0.1 N hydrochloric acid to the same indicator. Each milliliter of 0.1 N alkali consumed represents 18.0 mg. of acetylsalicylic acid.

(*k*) ***Other Esters; Fats:*** Several considerations applicable to the determination of esters by means of saponification have been discussed in Volume I (pp. 207–211). Fairly soluble compounds such as ethyl acetate and ethyl nitrite may be hydrolyzed easily in aqueous alkali, much as in the aspirin determination described above; a reflux condenser is necessary in case the ester is quite volatile.[83] In determining fats and other water-insoluble substances one generally employs an alcoholic solution of potassium or sodium hydroxide in the saponification step.

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[82] H. Boie, *Pharm. Ztg.*, **75**, 968 (1930); *Chem. Abstracts*, **25**, 169 (1931). P. S. Jorgensen, *J. Assoc. Official Agr. Chem.*, **21**, 555 (1938).

Since fats ordinarily contain some free fatty acids, it is customary to determine first the "acid number" (*cf.* p. 124). This is expressed as the number of milligrams of potassium hydroxide required for neutralization of the free acids contained in a one gram sample.[84] The "saponification number" represents the number of milligrams of potassium hydroxide necessary for saponification of the esters and neutralization of the free acids in a one-gram sample. The difference between acid and saponification numbers is called the "ester number."

Determinations of saponification number still follow quite closely the directions proposed originally by Koettstorfer.[85] An essential

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[83] For very volatile esters such as methyl formate one might use an apparatus such as that described by R. L. Busbey and N. L. Drake, *Ind. Eng. Chem., Anal. Ed.*, **10**, 390 (1938), for the hydrolysis of methyl bromide.

[84] According to N. Schoorl, *Pharm. Weekblad*, **52**, 724 (1915), it would be preferable to express all these quantities in terms of normality. Therefore he suggested that in each case the number of milliliters of 1 N alkali required for 100 g. of fat or oil should be reported, as follows: Acid norm (*Säurenorm*), S, for neutralization of the free acids. Saponification norm (*Verseifungsnorm*), V, for neutralization of the free acids and saponification of the esters. Ester norm, E, for saponification of the esters only. From these values one may calculate the mean molecular weight M of the fatty acids, assuming that no unsaponifiable material is present:

$$(M \times S) + (M + 12.7)E = 100{,}000$$

$$M = \frac{100{,}000 - 12.7E}{S + E}$$

The number 12.7 represents the equivalent weight of glycerin (92 ÷ 3) less the molecular weight of water, thus correcting for that part of the ester molecule which should not be included in the molecular weight of the acids. If unsaponifiable material were present in known quantity, the figure of 100,000 could be corrected by deduction of its weight (in mg. per 100 g.).

[85] J. Koettstorfer, *Z. anal. Chem.*, **18**, 199, 431 (1882). For further information concerning the analysis of esters, etc., see: G. H. Jamieson, *Vegetable Fats and Oils*, 2nd ed., Reinhold, New York 1943, pp. 371–467; H. G. Kirschenbauer, *Fats and Oils*, Reinhold, New York 1944, pp. 23–39; A. Grün, *Analyse der Fette und Wachse*, Springer, Berlin 1925.

condition for complete saponification is that sufficient alkali be present; not more than from one-half to two-thirds of the alkali should be consumed in the reaction.

Procedure: In a wide-mouth 250 ml. flask of resistant glass place 1.5 g. of the fat and 25 ml. of 0.5 N alcoholic potassium hydroxide (p. 72). Prepare also a blank with the same quantity of alkali. Fit both flasks with reflux condensers, being careful to avoid contamination of the solutions if cork or rubber stoppers are used. Heat on a boiling water bath for half an hour, or longer, if necessary, to dissolve all the fat. Cool under protection of a soda-lime tube and titrate with 0.5 N hydrochloric acid to phenolphthalein.

Notes: (1) If the alkali solution is made up in alcohol which contains aldehyde, it turns yellow and gradually diminishes in titer through formation of salts of organic acids. On this account, and also for the reason given below, it is advisable to run a blank with every set of determinations.

(2) Though a drainage error results from using for alcoholic alkali delivery a pipette that has been calibrated for water, the error is cancelled by measuring the alkali for the blank under exactly the same conditions.

(3) If the solution to be titrated is quite dark, thymol blue or ethyl bis-(2,4-dinitrophenyl) acetate may be used as indicator in place of phenolphthalein. Donath[86] suggested addition of barium chloride, whereupon a barium soap precipitates and carries down the colored substances; the mixture is then made to known volume and an aliquot part of the clear solution is titrated. This procedure introduces an error, since the barium soap also carries down some alkali. Pschorr, Pfaff, and Berndt[87] proposed to avoid the error by treating the saponified solution with an excess of 0.1 N acetic acid in alcohol, precipitating the soap with alcoholic calcium chloride, boiling, cooling, and titrating an aliquot portion of the water-diluted solution with alkali. Naturally such an indirect method is unattractive.

(4) Difficultly saponifiable fats or waxes may be hydrolyzed more rapidly with Rusting's alcoholic alkali-soap solution[88] or with sodium ethylate. In place of ethyl alcohol one may also use a higher boiling solvent such as isopropyl, butyl, or benzyl alcohol (*cf.* Vol. I, p. 209).

(5) Rieman[89] eliminates the need for running a blank by titrating the soap that is formed. After saponification, the excess of alkali is neutralized to phenolphthalein with hydrochloric acid. Then 10 ml. of benzene is added and the mixture is titrated with standard 0.5 N acid. Bromophenol blue serves as indicator and the end-point is a green color (in the aqueous phase) which does not revert to blue after swirling. The method fails if acids of low molecular weight, such as those from palm oil or acetylated products, are present.

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[86] E. Donath, *Chem. Rev. Fett- u. Harz-Ind.*, **12,** 74 (1905).

[87] R. Pschorr, J. K. Pfaff, and W. Berndt, *Z. angew. Chem.*, **34,** 334 (1921).

[88] N. Rusting, *Pharm. Weekblad,* **45,** 433 (1908). N. Schoorl, *ibid.*, **52,** 724 (1915). Preparation of the solution is described in Vol. I of this text, p. 210.

[89] W. Rieman III, *Ind. Eng. Chem., Anal. Ed.*, **15,** 324 (1943).

C. QUANTITATIVE PRECIPITATION AND COMPLEX-FORMATION REACTIONS

CHAPTER VIII

ARGENTOMETRIC TITRATIONS

1. Introduction.—The theoretical aspects of quantitative precipitations, including titration curves, adsorption phenomena, and the calculation of titration errors, have been treated in Vol. I (pp. 31–45, 58–67, 96–98, 143–146). The material presented here will be limited to practical details about the more important titration procedures, with especial consideration for methods of locating the end-points.

In a discussion of precipitation methods it is convenient to distinguish between *direct titrations*, in which standard solution is added to a solution of the substance being determined until the end-point is reached, and *indirect titrations*, in which an excess of the precipitant is added and the excess is back-titrated. Direct titrations are to be preferred, but they cannot always be applied. For example, if the solubility of the precipitate is too large one cannot detect the equivalence-point accurately. In such a case the solubility of the precipitate may be repressed by addition of excess reagent. The resulting suspension is made up to a definite volume and filtered without washing, after which the excess of reagent is determined by back-titration of an aliquot portion of the filtrate. Use is made of this method in the determination of the silver number (Kirschner's number) of volatile fatty acids.

In direct titrations the end-point may be detected in various ways. The precipitant may be added until a further addition does not cause a precipitate to appear in the solution, which is cleared each time by filtering or centrifuging, or merely by allowing the suspension to settle. The determination of silver by the Gay-Lussac method[1] is based on this principle. Such a method does not always yield entirely accurate results. Mulder[2] showed by his studies on the accuracy of the silver determination that a saturated silver chloride solution gives a slight precipitation upon the addition of a solution of either silver or chloride ion. Therefore, if one titrates a silver solution with a sodium chloride solution until a further addition no longer gives rise to a turbidity, the equivalence-point will have been passed. The empirical end-point in the Gay-Lussac method occurs a little after the equivalence-point. The corresponding error in the determination can be compensated by an equal error in the standardization only if the conditions of volume, concentration, temperature, and acidity are identical in the two cases.

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[1] J. L. Gay-Lussac, *Instruction sur l'essai des matières d'argent par la voie humide.* Paris 1832 (German translation 1833).

[2] G. J. Mulder, *Scheikundige Verhandelingen en Onderzoekingen.* Vol. I, Utrecht. German translation (by Grimm), Weber, Leipzig 1859.

The equivalence-point for the determination can, however, be found accurately. A saturated silver chloride solution gives with an excess of chloride a precipitate of the same character as that produced by an equal excess of silver nitrate (Vol. I, pp. 31–34, 98). Mulder made this the basis for a determination of silver which has long found application in the Netherlands mint laboratory (*cf.* p. 296). The standard solution is added until the supernatant liquid gives with a certain quantity of silver nitrate the same turbidity as with an equal quantity of chloride. In extremely accurate work it is necessary to wait a long time for the opalescence to develop. According to the investigations of Richards and Wells,[3] the presence of electrolytes hastens the precipitation. In their work on the revision of the atomic weight of sodium and of chlorine, Richards and Wells employed this method and recommended that a nephelometer[4] be used for the accurate comparison of opalescences. Since this instrument measures reflected rather than transmitted light, its use brings about an appreciable refinement.

In case the precipitate does not settle readily toward the end of the titration, it can be filtered off after each addition of reagent and the filtrate examined. In 1828, Gay-Lussac[5] described such a procedure for the determination of barium with a sulfate solution. The method is obviously very tedious.

Precipitates which have a tendency to remain in colloidal dispersion usually flocculate near the equivalence-point (*cf.* Vol. I, p. 190).

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[3] T. W. Richards and R. C. Wells, *Z. anorg. Chem.*, **47**, 56 (1905); *J. Am. Chem. Soc.*, **27**, 459 (1905).

[4] T. W. Richards and R. C. Wells, *Am. Chem. J.*, **31**, 235 (1904); **35**, 99, 510 (1906).

[5] J. L. Gay-Lussac, *Ann. chim. phys.*, **39**, 352 (1828). See also R. Wildenstein, *Z. anal. Chem.*, **1**, 432 (1861). G. Brügelmann, *ibid.*, **16**, 19 (1877). N. Tarugi and G. Bianchi, *Gazz. chim. ital.*, **36**, I, 347 (1906).

Before this point is reached, a small amount of the ion which stabilizes the sol is present and the supernatant liquid is more or less strongly opalescent. At the equivalence-point, however, where the stabilizing ion has been completely removed, flocculation becomes complete and after vigorous shaking the liquid over the precipitate becomes perfectly clear. In this case, therefore, it is possible to titrate to a "clear-point." This method gives good results, especially in the determination of iodide with silver nitrate. Excess iodide holds the silver iodide in colloidal suspension until the equivalence-point is approached, at which time the solid first begins to flocculate. Under certain conditions the precipitate may adsorb iodide ions, causing the clear-point to appear a little too early. With vigorous shaking and greater dilution, however, good results are possible[6] (*cf.* p. 273). Since the solubility of silver iodide is extremely small (approximately 0.0025 mg. per liter), a saturated solution gives no further precipitate upon the addition of either silver or iodide ions.

A practical application of titrating to a clear-point has been made by Sacher[7] in the titration of lead nitrate with molybdate. This is carried out in a hot solution containing acetic acid and acetate ions.

As long as an excess of lead is present, addition of molybdate solution causes precipitation of lead molybdate and the supernatant liquid remains turbid. If the titration is made dropwise near the end-point, and if the lead molybdate is allowed to settle one or two minutes after each addition, a point is finally reached at which the solution suddenly becomes clear. This point corresponds closely to the equivalence-point. It is obvious that the original lead solution must be free from any other turbidity. A turbid solution should first be filtered or centrifuged.

As a general rule the equivalence-point is detected with the aid of an added indicator. If the indicator is so sensitive that it reacts with the precipitate, the end-point appears too soon. Good results may still be obtained in some cases by employing the *spot method.* After each addition of reagent a drop of the titrated solution is tested with a suitable indicator. The spot method is applied, for example, in the determination of zinc with sodium sulfide using lead acetate paper, or in the determination of phosphate with uranyl solution using potassium ferrocyanide either on a spot plate or as an indicator paper. The drop removed for the test should be perfectly clear. If it contains a small amount of suspended precipitate, the latter may react with the indicator. In the determination of phosphate with uranyl solution, for example, the author has observed that the precipitate settles with difficulty and that several drops have to be withdrawn to assure getting a clear one. If a turbid drop is used in the test the end-point comes too early and lacks sharpness. In experienced hands the spot method gives good results and it has been found useful in certain industrial laboratories. For general laboratory work, however, it is rarely employed.

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[6] See also A. Lottermoser, W. Seifert, and W. Forstmann, *Kolloid-Z.* (*Zsigmondy Festschrift*), **36**, 230 (1925).

[7] J. F. Sacher, *Kolloid-Z.*, **19**, 276 (1926).

2. General Methods of Argentometric Titration; Indicators.—There are several methods which find fairly general application in argentometric halide and thiocyanate determinations:

(*a*) *Mohr method* with potassium chromate as indicator: A direct titration with silver nitrate to a faint red-orange color.

(*b*) *Fajans method* with an adsorption indicator such as fluorescein, dichlorofluorescein, or eosin: A direct titration with silver nitrate.

(*c*) *Volhard method*: An indirect method in which the halide is quantitatively precipitated with an excess of silver nitrate and the latter is determined in acid medium by back-titration with thiocyanate using ferric ion as indicator.

(A) METHOD OF MOHR

This well known titration of halides with silver nitrate, using potassium chromate as indicator, was first described by Mohr[8] in 1856, and has been examined repeatedly in the literature. It is especially useful for the determination of chloride. After all the chloride has been precipitated as silver chloride, the indicator forms a red precipitate of silver chromate with an excess of the silver solution. The theory of this titration, including the titration error, has been discussed in Volume I (pp. 144–146). The titration error depends primarily upon the sensitivity of the indicator toward silver ions. This may be theoretically derived from the solubility products but is better determined experimentally.

Sensitivity of the Indicator toward Silver Ions: The sensitivity is dependent on various factors such as the chromate concentration, temperature, hydrogen-ion concentration, concentration of electrolytes, and manner of observing the red coloration. Experimentally the sensitivity is determined by the quantity of standard silver solution necessary to cause a slight but distinctly perceptible color change. The sensitivity varies with the observer and always corresponds to a higher concentration of silver than is theoretically deduced. An appreciable amount of solid silver chromate must be formed before its color can be observed.

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[8] F. Mohr, *Ann.*, **97**, 335 (1856).

The literature makes divergent recommendations concerning the proper quantity of indicator.[9] In agreement with Tillmans and Heublein, and with Winkler,[9] the authors found that 1 or 2 ml. of a 5% potassium chromate solution per 100 ml. of liquid is satisfactory. This corresponds to a chromate concentration of 5×10^{-3} molar. Since the solubility product of silver chromate is approximately 2×10^{-12} at room temperature, this quantity of chromate requires theoretically that the concentration of the silver ions exceed 2×10^{-5} N to yield silver chromate.

The sensitivity may be determined experimentally by placing the indicator and 100 ml. of distilled water in each of two beakers; 0.01 N silver nitrate is then added to one beaker until a distinct difference of color (visible in daylight) is apparent. Thus the sensitivity is found to be 3 or 4×10^{-5} N for the silver ion, corresponding to a p_{Ag} of 4.5–4.4.

The author repeated the above experiment after adding 300 mg. of freshly prepared silver chloride and found that the sensitivity is practically unaffected by the presence of the precipitate.

With rising temperature the solubility product of silver chromate increases; hence the sensitivity toward silver ion decreases.[10] The following table gives values for the sensitivity at several temperatures. In order to obtain good results with the Mohr titration it is necessary to work at room temperature.

SENSITIVITY OF CHROMATE FOR SILVER ION AT VARIOUS TEMPERATURES

(100 ml. of water, 2 ml. of 5% potassium chromate)

Temperature, °C.	Sensitivity, *moles Ag per liter*
20	3×10^{-5}
40	4×10^{-5}
60	9×10^{-5}
70	15×10^{-5}
80	19×10^{-5}

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[9] J. Tillmans and O. Heublein, *Chem.-Ztg.*, **37**, 901 (1913). L. W. Winkler, *Z. anal. Chem.*, **53**, 359 (1914). O. Mayer, *ibid.*, **54**, 147 (1915). W. Herbig, *Z. angew. Chem.*, **32**, 216 (1919). I. M. Kolthoff, *Z. anal. Chem.*, **56**, 498 (1917). L. Yoder, *Ind. Eng. Chem.*, **11**, 755 (1919). H. W. van Urk, *Z. anal. Chem.*, **67**, 281 (1925).

[10] *Cf.* L. L. de Koninck and E. Nihoul, *Z. angew. Chem.*, **4**, 295 (1891).

The significance of the hydrogen-ion concentration has been investigated frequently. Since silver chromate is soluble in acids, the solution being titrated must be very nearly neutral. In experiments with buffers the author has shown that a hydrogen-ion concentration of 5×10^{-7} should not be exceeded, that is, the p_H should not be less than 6.3.

On the other hand the solution must not be too strongly alkaline, as silver hydroxide is also a slightly soluble compound. With a large concentration of hydroxyl ions the solubility of silver hydroxide may be exceeded before that of silver chromate. From the author's experience the p_H must remain below 10.5, that is, the solution must not react alkaline to nitramine or tropeolin O. Acid solutions may be neutralized conveniently by adding an excess of chloride-free borax, sodium or potassium bicarbonate, calcium carbonate, or magnesium oxide.[11] Borax and bicarbonate are especially recommended. Sodium carbonate, however, should not be used, as a relatively small concentration of carbonate ions interferes by forming slightly soluble silver carbonate.

Effect of Salts: It is the author's experience that even large quantities of alkali nitrates, sulfates, bicarbonates, biborates, or acetates, have no effect on the sensitivity of the chromate indicator. On the other hand, phosphates (formation of silver phosphate), arsenates, sulfites, sulfides, and fluorides interfere strongly. Sulfite may be rendered harmless by oxidation to sulfate. Hydrogen sulfide may be removed by boiling or by precipitating with zinc acetate.

Ammonium salts of strong acids do not affect the sensitivity. However, if an acid solution containing an ammonium compound is neutralized with sodium bicarbonate until a p_H of approximately 8 is reached, so much ammonia is formed that the end-point comes too late. In the presence of ammonium salts a p_H between 6.5 and 7.2 should be maintained.

Summary: From 1 to 2 ml. of a 5% solution of potassium chromate should be allowed for each 100 ml. of suspension present at the end-point. If the titration is continued until the first perceptible red-brown coloration, an excess of silver ion corresponding to a concentration of $3\text{–}4 \times 10^{-5}$ M is present.

The titration should not be made at an elevated temperature; the p_H should lie between 6.5 and 10.5. Acid solutions may be neutralized conveniently with borax or bicarbonate. In the presence of ammonium salts a p_H between 6.5 and 7.2 should be maintained. Anions which form slightly soluble salts with the silver ions interfere in the titration.

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[11] I. M. Kolthoff, *Z. anal. Chem.*, **56**, 499 (1917).

(B) METHOD OF FAJANS

The behavior of adsorption indicators has already been discussed in Vol. I (p. 102). Fluorescein, dichlorofluorescein, and eosin have been used extensively as indicators, and in addition several other compounds have been recommended for different titrations. The dye anion is not especially sensitive to the silver ion, but is adsorbed by the silver halide and in the process of adsorption undergoes a characteristic color change. A substance can be used as an indicator only if it is adsorbed appreciably in the immediate vicinity of the equivalence-point. Eosin is not applicable, for this reason, to the determination of chloride. Chloride ions are so readily displaced from the surface of silver chloride by eosin that the color change occurs at the beginning of the titration. Silver bromide, iodide, and thiocyanate, on the other hand, adsorb the corresponding negative ions so strongly that these ions are not displaced by eosin until the equivalence-point is reached or just passed.

Attention must be given to the fact that the sensitivity of a silver halide toward light is greatly increased (sensitization) by these dyes. The titration must be made rapidly, and in diffused light rather than in direct sunlight. Fajans and Wolff[12] have also pointed out that at least a portion of the precipitate formed in the titration must remain as a sol if a sharp end-point is to be obtained. The presence of large quantities of electrolytes, especially multivalent cations, causes interference. This limitation is especially important in the use of eosin; fewer difficulties are encountered with fluorescein or dichlorofluorescein.

Fluorescein as Indicator: A stock solution is prepared by dissolving the sodium salt of fluorescein in water so as to make a 0.2% solution; a 0.2% solution of fluorescein in alcohol may also be used. Fajans and Wolff recommend the use of 1–2 drops of indicator for 10 ml. of neutral 0.1 N halide. Reference solutions cannot be used as the flocculated precipitate is rapidly decomposed by light.

The phenomena that occur during a titration are dependent upon the concentration of the halide solution used. If a 0.1 N solution of chloride is being titrated, the sol flocculates about 1% before the equivalence-point. The titration is continued, with vigorous agitation, until the precipitate that separates suddenly acquires a reddish color. Although the color change on the flocculated solid is readily observed, the author has shown that the precipitate may be held in colloidal suspension by the addition of 5 ml. of a 2% solution of chloride-free dextrin which acts as a protective colloid. A sharp color change is then observed throughout the entire volume. In the titration of more dilute solutions, without dextrin, the coagulation coincides with or may shortly follow the color change.

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[12] K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

The determination gives exact results in the titration of chloride, bromide, iodide, and thiocyanate. The titration error is small and may generally be neglected.[13] Although large quantities of neutral salts ordinarily do not interfere, multivalent cations, such as the alkaline earth ions, bring about early coagulation and render the end-point indistinct.[14] In general the end-point is sharper than that of the Mohr titration. According to the authors' experience, however, the method is no longer useful for very dilute solutions of chloride (less than 0.005 N). Therefore in such procedures as the analysis of drinking water it cannot replace the Mohr titration.

The solutions should not be higher in acidity than those for the Mohr titration. The author has sought for other indicators which would be useful in slightly acid media.[15] In the presence of only a small amount of acetic acid, tropeolin OO, metanil yellow, and bromophenol blue may be used satisfactorily.

In titrations using metanil yellow and tropeolin OO, the color of the flocculated silver chloride changes suddenly at the equivalence-point from white to pale rose. The end-point is not so sharp as with fluorescein in neutral solution. The color change may be seen somewhat better with metanil yellow than with tropeolin OO. From 3 to 5 drops of a 0.2% aqueous solution are required for 25 to 100 ml. of chloride solution. The error is approximately 0.2%. The indicator is applicable to the direct argentometric titration of solutions of the chlorides of such metals as zinc, copper, and aluminum.

Alkaloid chlorides may be titrated more accurately using the sodium salt of bromophenol blue as indicator. For 25 to 100 ml. of solution are added 3–5 drops of 0.1% aqueous indicator solution and enough 4 N acetic acid to produce a greenish yellow color. The solution is titrated with silver nitrate until the color of the flocculated silver chloride suddenly becomes greenish blue or blue. Although the end-point is not so sharp as with fluorescein, the equivalence-point may be located to within 0.2%. The precipitate formed during the titration of an alkaloid chloride acquires a greenish color long before the end-point, but at the equivalence-point the color changes suddenly to a blue.

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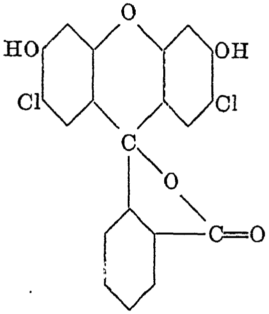
[13] For the error in chloride titrations, see W. Böttger and K. O. Schmitt, *Z. anorg. allgem. Chem.*, **137**, 246 (1924); also I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, 70, 369 (1927).

[14] H. Menzel, *Z. Elektrochem.*, **33**, 68 (1927).

[15] I. M. Kolthoff, *Z. anal. Chem.*, **71**, 235 (1927).

Bromophenol blue may also be used to advantage for titrating mixtures of iodide and chloride.[15]

Dichlorofluorescein as Indicator: For use in weakly acid solutions dichlorofluorescein is more suitable than the aforementioned indicators. It is available commercially or may be prepared from monochlororesorcinol and phthalic anhydride.[16] Some commercial products have no value as indicators, however, probably because the chlorine atoms are substituted in the phthalic acid ring.



Dichlorofluorescein

Indicator Solution: A 0.1% solution in 60–70% alcohol, or a 0.1% solution of the sodium salt in water, is satisfactory. Approximately 2.5 ml. of 0.1 N sodium hydroxide will neutralize 100 mg. of the indicator.

Procedure: Two drops of indicator solution are added to 10 ml. of chloride solution before it is titrated with silver nitrate. About 0.5% before the equivalence-point the silver chloride flocculates. The titration is continued by the dropwise addition of silver nitrate until the end-point, evidenced by a sudden change to red, is reached.

Notes: (1) The chloride concentration must not be greater than 0.025 N.

(2) Very dilute chloride solutions can be titrated with reasonable accuracy. As the end-point is approached the solution assumes a brown color and when the equivalence-point is reached the color changes suddenly to an orange. A very slight excess of silver produces a decided rose or red color. If an excess of silver is used, it may be back-titrated satisfactorily provided the latter titration is made without delay. In the titration of dilute solutions the optimum amount of indicator is 2–4 drops per 50 ml. of solution. Samples which are only 0.0005 N in chloride may be analyzed with an accuracy of 1 to 2%.

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[16] I. M. Kolthoff, W. M. Laur, and C. J. Sunde, *J. Am. Chem. Soc.*, **51**, 3273 (1929).

(3) The indicator can also be used in slightly acid solutions of p_H greater than 4. The chlorides of copper, zinc, manganese, nickel, aluminum, calcium, strontium, barium, and magnesium in 0.025 N solutions can be accurately titrated with silver nitrate in spite of the fact that the silver chloride may flocculate when only 50–80% of the silver solution has been added.

(4) Bromide and iodide even in very dilute solutions can be determined using dichlorofluorescein. The indicator may also be used for determining the sum of chloride and iodide in a mixture.

Eosin as Indicator: The titrations with eosin as indicator are of considerable importance. Bromide, iodide, and thiocyanate, even in dilute solutions, may be titrated accurately. In addition, the solutions may be moderately acid, in some cases as high as 0.1 N in nitric acid. According to the authors' experience, a weakly acid reaction enhances the color change; it is desirable to treat neutral solutions with a little acetic acid before titrating.

Indicator Solution: The eosin solution is made up to contain 0.5% of the sodium salt in water. Fajans and Wolff[12] recommend 2–5 drops of indicator per 10 ml. of 0.1 N halide solution; they regard the change as less sharp than that obtained with fluorescein.

Kolthoff and van Berk,[13] however, were able to titrate halide solutions with an accuracy of 0.1%, after adding acetic acid. The same accuracy was realized in the titration of thiocyanate. They employed 1–3 drops of indicator per 10 ml. of 0.1 N solution. In the titration of stronger halide solutions (0.1 N) the same phenomena are encountered as those described under the fluorescein titration. About 1% before the equivalence-point the halide flocculates and the titration is continued with vigorous shaking until the precipitate suddenly turns an intense red color. This change frequently coincides with the "clear-point." The addition of a protective colloid does not improve the end-point.

Very dilute bromide, iodide, and thiocyanate solutions may be titrated accurately in either neutral or acetic acid medium. In the titration of 0.01 N solutions the color of the indicator changes toward blue as the end-point is approached, but at the equivalence-point the solid suddenly separates out with a rose red color. For 25 ml. of 0.01 N solution, 1 or 2 drops of indicator usually suffices. In the titration of a 0.001 N solution the coagulation can no longer be detected, but the color change from a rose to a purplish red is distinct. In acetic acid solution the end-point is very sharp and the determination is still accurate to 0.5%.

Phenosafranine as Indicator: Berry and Durrant[17] pointed out that phenosafranine is a good adsorption indicator for the titration of chloride and bromide solutions. The dye is a green crystalline product which dissolves in water to give a bright red solution. During the titration of chloride or bromide with silver nitrate most of the indicator is adsorbed on the precipitate in its red form; at the equivalence-point the color suddenly changes to blue. Berry and Durrant recommended the indicator for use in solutions as strong as 0.5 N in nitric acid. It is not useful in the presence of sulfuric acid because of a bleaching effect on the color. Berry later noted[18] that good results can be obtained only when the halogen is present in ionic form. Undissociated compounds such as chromic chloride, thallic chloride, and mercuric chloride cannot be analyzed by this procedure. The same is of course true of any adsorption indicator method.

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[17] A. J. Berry and P. J. Durrant, *Analyst,* **55**, 613 (1930).

Indo-oxine as Indicator: According to Berg and Becker[19] the compound 5,8-quinolinequinone-8-hydroxy-5-quinolyl-5-imide (which is designated as indo-oxine) has a red color in acetate buffer and reacts with silver to form a blue-green precipitate. The sensitivity corresponds to about 0.4 mg. of silver per liter in neutral solution or to 4 mg. per liter in 0.04 N acetic acid. Several other metals, including copper, bismuth, mercury, nickel, and cobalt also form slightly soluble salts, so that the indicator is somewhat limited in applicability. It acts as an adsorption indicator in the titration of halides.

Titration of Chloride or Thiocyanate: For 50 ml. of solution one adds an equal volume of ethanol or acetone, 1–5 ml. of acetic acid and 1 ml. of a 0.05% solution of the indicator in alcohol. The mixture is then titrated with 0.1 N silver nitrate to a color change from red to blue. According to Berg and Becker, 0.001 N chloride solutions can be titrated in this way. The acidity should be properly adjusted, for at lower acidities the color change occurs before the equivalence-point. Bromide and iodide may be titrated in the same way or in neutral medium, as their silver salts are much less soluble than silver chloride.

Brilliant Orsella C and Chromotrope F4C as Indicators: Belladen and Piazza[20] recommend these compounds as adsorption indicators, stating that halide solutions as dilute as 0.003 N may be titrated with an accuracy of 0.2%. Brilliant Orsella C in the chloride titration gives a blue-green precipitate at the equivalence-point and the red solution is thereby rendered colorless. In the bromide titration the precipitate is colored a grayish green and with iodide there is a color change from violet-red to gray-green. Using Chromotrope as indicator for bromide titrations a color change from pink or violet in solution to a gray on the precipitate is produced. Iodide titrations give a change from pink to green, and in the presence of magnesium sulfate, the color of the silver iodide precipitate changes from yellow to green. Polyvalent cations generally interfere.

Iodide and chloride may be titrated in the same solution, according to Belladen and Piazza. When the ratio of potassium chloride to potassium iodide is equal to or less than unity, results virtually identical with the theoretical are obtained. When the ratio of potassium chloride to potassium iodide is three, the error is approximately 0.3%. The reverse titration of silver nitrate with potassium bromide solution using Brilliant Orsella C is possible in neutral solutions as well as in those containing up to 0.3 N nitric acid. At the equivalence-point a color change from bright green to pink is obtained.

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[18] A. J. Berry, *Analyst*, **57**, 511 (1932).

[19] R. Berg and E. Becker, *Z. anal. Chem.*, **119**, 81 (1940).

[20] L. Belladen and G. Piazza, *Ann. chim. applicata*, **22**, 631 (1932).

Diphenylcarbazone as Indicator: Chirnoagă[21] uses a 0.2% alcoholic solution of diphenylcarbazone (*cf.* p. 317). In the titration of chloride a color change from bright red to violet is obtained; with bromide and iodide the change is from yellow to green, and with thiocyanate from pink to blue.

Procedure: For 10 ml. of approximately 0.1 N solution to be titrated, 2 ml. of 0.4% starch solution and 5–8 drops of indicator are taken. Silver nitrate is then added until the end-point is reached.

Notes: (1) Since no color change is obtained in the presence of acid, an acid solution must be first neutralized. Applications of the indicator are limited as various compounds, including acetates and ammonium salts, interfere.

(2) The color change obtained upon addition of excess silver is reversible, but not if the mixture is allowed to stand long before back-titration.

(3) Agar-agar may be used in place of starch, but gelatin cannot be used.

(4) Chirnoagă has also suggested the use of a colloidal ferroferricyanide solution as indicator. When this indicator is added just before the end-point, the silver halide is colored a distinct blue, but at the equivalence-point the precipitate becomes colorless. This procedure is applicable only to neutral solutions and hence is of little practical importance.

p-Ethoxychrysoidine as Indicator: Schulek and Rózsa[22] titrate neutral iodide and thiocyanate solutions with silver nitrate using *p*-ethoxychrysoidine as indicator. The color change is from red to yellow.

Other Indicators: Among other adsorption indicators which have been proposed for use in argentometric titrations of halides or thiocyanates are bromocresol purple, Victoria violet and tetrahydroxyanthraquinone,[23] and *o*-cresolphthalein.[24] The use of diphenylamine blue is described on p. 258.

(c) METHOD OF VOLHARD

In the Volhard titration[25] an excess of standard silver nitrate solution is added to the halide solution and the excess silver is titrated in acid medium with standard thiocyanate, using ferric ammonium sulfate as indicator. The accuracy is determined primarily by the back-titration. Details of the procedure will be discussed later.

A ferric solution is a very sensitive indicator for thiocyanate ion. Generally 1–2 ml. of a saturated solution of ferric ammonium sulfate (approximately 40%) per 100 ml. of liquid gives the most satisfactory concentration. The exact acid content is not of great importance, provided it is at least 0.3 N. Nitric acid is ordinarily used but the sensitivity with sulfuric acid is practically the same. Under the conditions mentioned, a pale orange color is given by 0.1 ml. of 0.01 N thiocyanate per 100 ml. (corresponding to a thiocyanate concentration of 10^{-5} N). The indicator error is therefore negligible in the titration of 0.1 N solutions. In the use of the Volhard method, however, it must be realized that freshly precipitated silver thiocyanate adsorbs relatively large amounts of the silver ion.[26] On this account the first perceptible color change comes approximately 0.7-1% too soon. The titration must be continued with vigorous shaking until a permanent pale red-orange color is obtained. Under the best conditions a precision of 0.05% is then obtainable.

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[21] E. Chirnoagă, *Z. anal. Chem.*, **101**, 31 (1935).

[22] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **115**, 194 (1939).

[23] H. A. Pieters, *Chem. Weekblad*, **26**, 6 (1929).

[24] Y. Uzumasa and Y. Miyaki, *J. Chem. Soc. Japan*, **55**, 627 (1934); *Chem. Abstracts*, **28**, 6385 (1934).

[25] J. Volhard, *Ann.*, **190**, 1 (1878); *J. prakt. Chem.*, **9**, 217 (1874).

3. Primary Substances and Standard Solutions for Argentometry.—The standard substances for argentometry should conform to the general requirements mentioned in Chapter II. Fortunately several suitable materials are available. The purification and testing of some of these are described below.

Sodium chloride ($NaCl$, equivalent weight 58.45, rational 58.43): Analytical reagent grade material may ordinarily be used directly after drying, though it should first be tested for purity. Alternatively, hydrogen chloride may be passed into a saturated solution of commercial sodium chloride (not iodized). The salt thus precipitated is filtered by suction, washed several times with water, dried, and tested for purity. If it satisfies the qualitative requirements (except with respect to the acid reaction), the dried salt is heated to constant weight in a crucible over an alcohol flame or in an electric oven at a temperature of 500–600°C. A gas flame may be used if the crucible is placed on an inclined asbestos square so as to prevent contamination from sulfur-bearing gases. If the salt is not sufficiently pure it can be dissolved and reprecipitated with hydrogen chloride.

Tests for Purity. Water: 10 g. of salt should not lose more than 1 mg. (0.01%) on gentle ignition. Moisture may also be determined by the Sörensen method as described under sodium oxalate (p. 75).

Reaction: A solution of 1 g. of salt in 10 ml. of ordinary distilled water should give a transition color with methyl red. If this is obtained, not more than 0.002% hydrochloric acid is present.

Sulfate: A solution of 1 g. of the salt in 10 ml. of water should not give any precipitate of barium sulfate within 15 minutes after the addition of a little acetic acid and barium nitrate (sensitivity 0.01% Na_2SO_4).

Potassium: A solution of 0.5 g. of the salt in 10 ml. of water should not show any turbidity with 1 ml. of de Koninck's reagent (p. 81) and 10 ml. of alcohol, after standing 10 minutes. This test is sensitive to 0.005% KCl. Potassium chloride is an active impurity; 0.1% potassium chloride in sodium chloride lowers the effective strength by 0.022%.

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[26] *Cf.* C. Hoitsema, *Z. angew. Chem.*, **17**, 647 (1904). I. M. Kolthoff, *Z. anal. Chem.*, **56**, 568 (1917).

Calcium, Barium, and Magnesium: A solution containing 0.1 g. of sodium chloride per 10 ml. of water is treated with 0.4 ml. of 2 N sodium carbonate and 2 drops of 4 N sodium hydroxide, and is boiled in a Pyrex vessel. After cooling, no opalescence or precipitate should be apparent when viewed against a black background. Sensitivity, 0.01% Ca, Ba, or Mg.

Bromide and Iodide: To a solution of 0.1 g. of salt in 5 ml. of water is added one drop of a 0.1% fluorescein solution (in alcohol) and one drop of either chlorine water, 1% hypochlorite, or 1% chloramine T solution. The mixture is immediately made alkaline with ammonia. In transmitted light, against a white background, the solution should appear green; no rose coloration of eosin should be visible (sensitivity 0.005% Br or I).

Potassium Chloride (KCl, equivalent weight 74.55, rational 74.52): A good grade of the salt is recrystallized three times from water, dried, and heated to 500–600°C. as described under sodium chloride. Traces of bromide are not removed by recrystallization from water. To remove bromide the solid is first recrystallized from a 0.2% solution of potassium hypochlorite and then three times from pure water.

Tests for Purity: The tests are the same as those described above for sodium chloride, except that a test for sodium should replace that for potassium. 10 to 20 mg. of potassium chloride is heated on a clean platinum wire loop in a Bunsen flame. The flame should be pure violet; there should not be a transient yellow coloration even as the heating begins. Sensitivity, 0.01% Na.

Potassium Bromide (KBr, equivalent weight 119.01, rational 118.98): Recrystallized potassium bromate is carefully heated in a platinum dish over an alcohol burner, only a small portion being taken at a time. The salt decomposes violently into potassium bromide and oxygen. After the mass has cooled, the crystals are ground and heated as previously described under sodium chloride. If the salt has been prepared from very pure potassium bromate, further tests are superfluous.

Potassium Thiocyanate (KCNS, equivalent weight 97.17, rational 97.13): Kolthoff and Lingane[27] studied the preparation of pure potassium thiocyanate and its use in the standardization of silver solutions. A good grade of commercial material is recrystallized several times from water, ethanol, or methanol. Water is preferable since chloride is more easily removed by crystallization from water than from alcohol. A salt to which has been added 1% of potassium chloride still contains 0.6% of this impurity after three crystallizations from ethanol, but less than 0.005% after three crystallizations from water. The recrystallized thiocyanate is collected on a suction filter and dried over sulfuric acid in a desiccator. This product is very pure, but contains a trace of water which is removed by fusion. The fused compound does not absorb water if it is kept at a relative humidity of less than 50%; over anhydrous calcium chloride or potassium carbonate, therefore, the salt is perfectly stable. When placed in direct sunlight it gradually assumes a yellow color. This decomposition is avoided if the salt is kept in a brown bottle. In the fusing process a yellow color may also be produced, but the salt can be melted without decomposition in an atmosphere free from acid vapors. The water content of potassium thiocyanate is 0.02% after an hour or two at 150°C. The last traces of water are removed if the temperature is raised to 200° for 10 minutes. Prolonged heating at this temperature is not advisable, however, because the salt slowly gains weight (0.05% in 15 hours). Aqueous solutions of potassium thiocyanate are stable for an indefinite period.

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[27] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, **57**, 2126 (1935).

Tests for Purity. The tests for acidity or alkalinity, sulfate, calcium, barium, and magnesium are the same as for these impurities in sodium chloride (p. 251).

Water or Alcohol: 10 g. of potassium thiocyanate should not lose more than 1 mg. (0.01%) upon being heated at 200°C. for 10 minutes.

Chloride: 1 g. of the salt is dissolved in 50 ml. water and 20 ml. of chloride-free concentrated nitric acid is added. The solution is refluxed for 2 to 3 hours at 90–95°C. After cooling, 1 ml. of 0.1 N silver nitrate is added. No turbidity should appear (sensitivity 0.005%).

Ammonia: 1 g. of the salt is placed on a watch glass and mixed with 1 ml. of 4 N sodium hydroxide. The watch glass is covered with another of the same size and a piece of red litmus paper is placed between them. The litmus should not turn blue within 15 minutes (sensitivity 0.001%).

Silver Nitrate ($AgNO_3$, equivalent weight 169.89, rational 169.87): Silver nitrate may be prepared from metallic silver by various methods, which are described in handbooks on inorganic preparation. In all manipulations, such as evaporation and drying, the silver nitrate must be scrupulously protected from dust and from the action of light.

Silver nitrate of excellent quality is available commercially. Impure products may be purified by recrystallization from water containing a small amount of nitric acid. The crystals that separate may be collected conveniently on a sintered glass crucible, thereby avoiding contamination from threads of filter paper and traces of organic substances. The crystals are dried at 110°C., and then, with protection from light and dust, are heated for 15 minutes at 220–250° (melting point 208°). According to Richards and Forbes[28] silver nitrate is not decomposed by this treatment and may be heated for several hours without serious change in weight. However, according to N. Schoorl (private communication) a negligible trace of nitrite may be formed. Schoorl states that an anhydrous product may be obtained by keeping the salt in a molten condition for 5 minutes. If the melt is kept at a considerably higher temperature the product may be slightly decomposed, according to Rosa, Vinal, and McDaniel.[29] The metallic silver thus formed remains in colloidal suspension when the salt is dissolved in water (see below), and the solution becomes slightly basic. Small amounts of nitrite may also be formed.

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[28] T. W. Richards and G. S. Forbes, *J. Am. Chem. Soc.*, **29**, 816 (1907).

[29] E. B. Rosa, G. W. Vinal, and A. S. McDaniel, *Bull. Bur. Standards*, **9**, 524 (1913).

Tests for Purity. Water: 10 g. of silver nitrate should not lose more than 1 mg. (0.01%) upon heating for a quarter of an hour at 230–250°C. Unmelted preparations of Kahlbaum contain approximately 0.1–0.2% water, according to unpublished communications of Schoorl.

Metallic Silver, Organic and Insoluble Substances: A solution of 1 g. of the fused silver nitrate in 10 ml. of water must be perfectly clear. After the addition of 1 ml. of 50% nitric acid and 0.1 ml. of 0.01 N potassium permanganate the solution must remain pale rose after 5 minutes of standing (sensitivity about 0.01% of reducing substances). If the test is positive a blank should be run on the reagents.

According to Rosa, Vinal, and McDaniel,[29] metallic silver in the colloidal state is rapidly oxidized by permanganate. Organic substances, on the contrary, are oxidized more slowly. The latter may reduce silver nitrate at the fusion temperature, so that the presence of free silver in the melt may serve as a test for organic substances present in the original salt.

Free Nitric Acid and Silver Oxide: The solution of 0.5 g. of silver nitrate in 10 ml. of water should show a transition shade with methyl red (sensitivity 0.001% HNO_3). If the indicator has an alkaline color, it should assume its acid color, or at least a transition tint, upon the addition of 0.1 ml. of 0.01 N acid.

Nitrite: The solution of 0.01 g. of silver nitrate in 10 ml. of water must not become red upon standing 5 minutes after addition of a little α-naphthylamine, sulphanilic acid, and several drops of acetic acid (sensitivity approximately 0.01%).

Ammonium Salts: The solution of 0.2 g. of silver nitrate in 10 ml. of water is treated with 2 ml. of a 10% solution of sodium chloride and is filtered. The filtrate should not show an orange color with Nessler's reagent (sensitivity 0.005% NH_3).

Foreign Substances: A hot solution of 10 g. of silver nitrate in 300 ml. of water is treated (in the dark) with a hot solution of 30 ml. of 4 N hydrochloric acid in 200 ml. of water. The silver halide is filtered on ashless filter paper and the filtrate evaporated to dryness. The residue is taken up in a little water and again filtered. The filtrate is transferred to a weighed crucible, evaporated, and weighed. The residue should not amount to more than 1 mg. (1:10,000). A blank test is necessary.

Metallic Silver (Ag, equivalent weight and rational weight 107.88): The investigations of Richards and Wells[30] showed that silver of very high purity is obtained by the reduction of silver nitrate with ammonium formate:

$$2AgNO_3 + 2HCO_2NH_4 \rightarrow 2Ag + 2NH_4NO_3 + CO_2 + HCO_2H$$

The ammonium formate used is prepared by passage of ammonia into freshly distilled formic acid. Pure silver nitrate is then added and the silver formed is washed free from ammonium salts. It is fused in a stream of hydrogen in a boat made of calcium oxide (from a mixture of pure lime and calcium nitrate). According to Baxter and Parsons[31] the quantity of hydrogen dissolved in the silver is negligibly small, about 0.0006%.

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[30] T. W. Richards and R. C. Wells, *J. Am. Chem. Soc.*, **27**, 459 (1905). See also W. Ponndorf, *Z. anal. Chem.*, **84**, 289 (1931); C. W. Foulk and L. A. Pappenhagen, *Ind. Eng. Chem., Anal. Ed.*, **6**, 430 (1934). Silver of sufficiently high purity may also be prepared electrolytically.

The Standardization of Silver Nitrate Against Sodium Chloride: Although both silver nitrate and sodium chloride may easily be obtained pure, a standardization of one solution against the other is desirable. A *working titer* is thus obtained, which may then be corrected for the *titration error*. Sodium chloride is often used as a primary standard for the standardization of silver nitrate.

Mohr Method: A weighed quantity of sodium chloride is dissolved and diluted so that its concentration is approximately 0.1 N. 1 to 2 ml. of 5% potassium chromate is added for 50 ml. of solution. The chloride is then titrated with silver nitrate until a faint but perceptible red-brown coloration (in comparison with a reference solution) persists after vigorous agitation. The titration error amounts to approximately 0.2%.

Fajans Method: A weighed quantity of sodium chloride is dissolved and diluted to a concentration of approximately 0.05 N. It is then titrated with silver nitrate, using 3–5 drops of 0.1% fluorescein or dichlorofluorescein, until a sudden change to rose is obtained. The titration error is negligibly small.

The standardization of silver nitrate solutions may also be carried out against potassium chloride or bromide, using the method of either Mohr or Fajans. In the latter procedure eosin should be used as the indicator in the bromide titration (*cf.* p. 245).

The Standardization of Thiocyanate Solutions: If necessary, thiocyanate solutions are standardized against silver nitrate or pure silver (see p. 337 for the use of mercuric oxide). If silver is used, the metal is dissolved in chloride-free nitric acid, after which the oxides of nitrogen are boiled out. The silver nitrate solution, which should contain at least 5 ml. of 4 N nitric acid and 1 ml. of saturated ferric ammonium sulfate solution per 50 ml. of liquid, is titrated with the thiocyanate solution to the first perceptible reddish brown color. The titration is continued, with vigorous shaking, until this color persists. The indicator blank is extremely small and at most amounts to 0.02%.

Volhard titrations of atomic weight accuracy were carried out by Kolthoff and Lingane.[32] Using purified potassium thiocyanate and silver (or silver nitrate), they found the effective strength of the potassium thiocyanate to be between 100.01 and 100.05%, with 100.02 the average. The variations from the theoretical are very slight and for most purposes may be neglected. Pure potassium thiocyanate is therefore recommended for the standardization of silver solutions, if the accuracy need not be better than to within 0.05%.

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[31] G. P. Baxter and L. W. Parsons, *J. Am. Chem. Soc.*, **44**, 577 (1924).

[32] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, **57**, 2126 (1935).

The small magnitude of the observed variations results from a compensation of errors. In the first place, adsorption equilibrium is not reached during titration under the given conditions. Secondly, a slight decomposition of thiocyanate takes place even in the absence of air. A small amount of thiocyanate is apparently converted to cyanate, which in acid solution quickly decomposes to ammonium ions and carbonic acid. In all the determinations a trace of ammonium ions could be found in the supernatant liquid. The error resulting from these side reactions is approximately 0.08%, and thus the strength of the potassium thiocyanate is 99.92% instead of 100.02%. This difference of 0.1% from the experimental value is explained by the presence of adsorbed or occluded silver. If the precipitate that is present near the end-point is allowed to digest overnight, it changes to such an extent that its adsorbing properties are virtually completely lost. If the titration is continued after the digestion, the effective value of the potassium thiocyanate is found to be 99.92 to 99.94%.

The Volhard method is not recommended for highly accurate standardizations but is useful for determinations demanding ordinary accuracy.

4. Argentometric Determinations of Halides, Thiocyanate, and Cyanide.

DETERMINATION OF CHLORIDE

(*a*) *Mohr Method:* The practical details of this determination have already been discussed on pages 242–245. If the solution contains a large quantity of electrolyte, the silver chromate that is formed by local excesses of reagent has a marked tendency to agglomerate. It then reacts very slowly with the chloride ions which are still present in excess, so that the end-point is often observed too early. Under these conditions it is necessary to shake vigorously near the equivalence-point and to titrate until the red-brown color no longer disappears after the mixture has been shaken and then allowed to stand for a short time.

In concentrated chloride solutions the end-point appears too soon and is not sharp, according to Lottermoser and Lorenz.[33] They note that the disturbance can be eliminated by addition of 5 to 10 ml. of 0.1% agar solution, which prevents the precipitate from agglomerating in large lumps.

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[33] A. Lottermoser and W. Lorenz, *Kolloid-Z.*, **68**, 201 (1934).

The Mohr method is of great importance for the titration of chloride in very dilute solutions, such as drinking water and solutions of technical products which may contain traces of chloride as an impurity. The reverse titration, that of silver with chloride, does not give good results with chromate as indicator; flocculated silver chromate reacts too slowly with the chloride being added and the end-point appears too late.

Determination of Chloride in Water: The reaction of the water toward neutral red, phenol red, or rosolic acid is first tested.[34] If it is definitely acidic, some sodium or potassium bicarbonate, borax, or calcium carbonate is added. If the water has a p_H greater than 6.8, it may be used directly for the titration. The p_H of natural water rarely exceeds 10.5. To 100 ml. of water, treated with bicarbonate if necessary, are added 1–2 ml. of 5% potassium chromate. The solution is titrated with 0.01 N silver nitrate to the first pale red-brown coloration. It is then diluted with distilled water to 150 ml. and again titrated to the end-point. As a reference liquid it is best to use a sample that has already been titrated and treated with a slight excess of chloride. Using this technique, the final volume is always the same, and according to Kolthoff[35] a correction of 0.6 ml. of 0.01 N silver nitrate should always be deducted. Winkler[36] titrates with a solution containing 4.791 g. of silver nitrate per liter, 1 ml. of which corresponds to 1 mg. of chloride. He also recommends the use of a reference solution of the type described above and titrates to the first perceptible color which does not diminish after standing for 5 minutes. Winkler then applies corrections as given in the table below.

CORRECTIONS FOR THE MOHR TITRATION, ACCORDING TO WINKLER

Silver Nitrate Solution Used, *ml.*	Correction, *ml.*	Silver Nitrate Solution Used, *ml.*	Correction, *ml.*
0.2	−0.13	1.0	−0.16
0.3	−0.13	2.0	−0.17
0.4	−0.14	3.0	−0.18
0.5	−0.15	4.0	−0.18
0.6	−0.15	5.0	−0.19
0.7	−0.15	10.0	−0.20
0.8	−0.16	15.0	−0.21
0.9	−0.16	20.0	−0.22

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[34] A. J. Berry and J. E. Driver, *Analyst*, **64**, 730 (1939).

[35] I. M. Kolthoff, *Z. anal. Chem.*, **56**, 498 (1917).

[36] L. W. Winkler, *Z. anal. Chem.*, **53**, 359 (1914).

Samples of water which are highly colored with organic matter, or which contain hydrogen sulfide, are first treated with an excess of potassium permanganate. After standing for 15 minutes the excess permanganate is reduced by the addition of sufficient chloride-free perhydrol The solution is then filtered and an aliquot portion of the filtrate is titrated as has been described (see also p. 244).

(*b*) ***Fajans Method:*** Fluorescein or dichlorofluorescein is used as indicator; the latter is preferable for several reasons as previously explained (p. 247).

For the titration of semimicro quantities of chloride or bromide in organic substances (after combustion), Hölscher[37] used 60% ethanol as a medium for the precipitation. He obtained an accuracy of 1% even with 0.001 N chloride. Dichlorofluorescein was used as indicator for the titration of chloride and eosin for that of bromide.

Bambach and Rider[38] used dichlorofluorescein for the titration of organic base hydrochlorides in alcoholic medium. The indicator, according to Bullock and Kirk,[39] may also be used in the microdetermination of chloride. The latter workers applied the titration to the determination of potassium. After precipitating this element as the chloroplatinate and reducing the precipitate with magnesium, they titrated the liberated chloride.

Tananaeff[40] has applied the chloride titration, with dichlorofluorescein as indicator, to the determination of lead or of fluoride after precipitation as lead chlorofluoride (p. 270).

Lang and Messinger[41] used diphenylamine blue as adsorption indicator for the determination of chloride and bromide in strongly acid solution. In acid solution the dye is in the cation form and is adsorbed by the negatively charged silver halide precipitate. During the early stages of a chloride titration the dye is completely adsorbed by the silver chloride, giving the precipitate a green color. As the titration is continued, the spot where the silver enters the solution assumes a violet color, until at the equivalence-point the entire solution turns violet. Upon further addition of silver, the color of the solution becomes deeper until all of the dye has been removed from the precipitate. The color change at the end-point is reversible. Near the end-point one should titrate carefully and watch for the clear-point.

Procedure: The indicator solution is prepared by adding 3 drops of a 1% solution of diphenylamine in concentrated sulfuric acid to 10 ml. of 5 N sulfuric acid and 1 ml. of 0.1 N potassium dichromate. This mixture should be prepared freshly as needed, since diphenylamine blue is not stable.

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[37] F. Hölscher, *Z. anal. Chem.*, **96**, 308 (1934). See also Y. Uzumasa and Y. Miyake, *J. Chem. Soc. Japan*, **53**, 904 (1932); *Chem. Abstracts*, **27**, 244 (1933).

[38] K. Bambach and T. H. Rider, *Ind. Eng. Chem., Anal. Ed.*, **7**, 165 (1935).

[39] B. Bullock and P. L. Kirk, *Ind. Eng. Chem., Anal. Ed.*, **7**, 178 (1935).

[40] I. Tananaeff, *Z. anal. Chem.*, **99**, 18, 21 (1934).

[41] R. Lang and J. Messinger, *Ber.*, **B63**, 1429 (1930).

To 25–40 ml. of approximately 0.1 N chloride solution add 10 ml. of indicator. The solution is shaken vigorously while being titrated with 0.1 N silver nitrate and the titration is continued until a permanent violet color appears. If the volume is more than 40 ml., a solution of 0.5 g. of barium nitrate should be added before titrating. However, it is advisable to keep the volume small and the acidity below 1 N in sulfuric acid.

Notes: (1) The titration gives excellent results for chloride or bromide in strongly acid solutions. Iodide, thiocyanate, and cyanide, however, cannot be determined by this method. Iodide and thiocyanate reduce diphenylamine blue, while silver cyanide continues to adsorb this compound even after the equivalence-point has been reached. Chloride solutions as dilute as 0.01 N can be titrated in the same way, except that a smaller amount of indicator (1 ml.) is used. An indicator containing 0.2 to 0.5 ml. (instead of 1 ml.) of 0.1 N potassium dichromate in 10 ml. of 5 N sulfuric acid, produces a good end-point. With more dilute chloride solutions, however, accurate results are impossible because the change is not sharp and comes too late.

(2) The titration may be carried out in the presence of acids such as hydrofluoric, phosphoric, oxalic, and acetic. No interference is caused by the salts of most heavy metals (Cr, Ni, Co, Cu, Pb, As, Bi); antimony and stannic salts are also without influence if tartaric acid or pyrophosphate is added.[42]

(*c*) ***Volhard Method:*** The chloride solution is treated with an excess of standard silver nitrate, which is back-titrated with standard thiocyanate. The method has the decided advantage over the Mohr method of being applicable in acid solution. However, the proper experimental conditions must be observed if accurate results are desired.

Drechsel[43] first called attention to the fact that thiocyanate acts upon silver chloride:

$$AgCl + CNS^- \rightleftarrows AgCNS + Cl^-$$

Upon back-titrating the excess of silver nitrate with thiocyanate, both silver chloride and silver thiocyanate are present in the solid phase. When equilibrium is reached between the solid phases and the solution saturated with both compounds, the following expression holds:

$$\frac{[Cl^-]}{[CNS^-]} = \frac{S_{AgCl}}{S_{AgCNS}} = \frac{1.12 \times 10^{-10}}{6.84 \times 10^{-13}} = 164$$

From this ratio it follows that in the back-titration of silver with thiocyanate the end-point cannot be sharp, since the excess of thiocyanate necessary to produce a color change will react with the solid silver chloride. The entire problem has been studied by Rosanoff and Hill.[44] For example, upon treatment of 100 ml. of a saturated silver chloride suspension with 0.1 ml. of 0.1 N thiocyanate solution, equilibrium is attained when the ratio of chloride to thiocyanate becomes 164. The increase in chloride concentration, x, is equal to the decrease in thiocyanate concentration. In a saturated solution of silver chloride the chloride concentration is 1.06×10^{-5} N, while the thiocyanate added corresponds to a concentration of 10^{-4} N. At equilibrium, therefore:

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[42] R. Lang and J. Messinger, *Z. anal. Chem.*, **88**, 336 (1932).

[43] E. Drechsel, *J. prakt. Chem.*, **15**, 191 (1877).

$$\frac{1.06 \times 10^{-5} + x}{10^{-4} - x} = 164 \qquad x = \frac{164}{165} \times 10^{-4}$$

The decrease in solubility of silver chloride resulting from the excess of chloride has been neglected here for the sake of simplicity.

This calculation shows that at equilibrium approximately 164/165 of the added thiocyanate reacts with silver and only 1/165 remains. Therefore after an addition of enough thiocyanate to make its normality 10^{-4} assuming no reaction, the concentration remaining at equilibrium is only $1/165 \times 10^{-4}$ N. Since a concentration of 10^{-5} N is needed to produce a perceptible color with ferric ions (p. 251), one can calculate that 1.65 ml. of 0.1 N thiocyanate must be added to 100 ml. of silver chloride suspension in order that the color should no longer disappear after shaking. The author established[44] that in practice about 2.5 ml. of 0.1 N solution are necessary.

Various workers have called attention to the above sources of error in Volhard titrations and have proposed modifications, including filtration before the back-titration. Volhard[45] maintained that the action of thiocyanate upon silver chloride is slow enough so that filtration is unnecessary, but Rosanoff and Hill[44] demonstrated that the action is quite rapid. They as well as Drechsel[43] recommended the filtration procedure. Another error may be involved here if the precipitate is filtered off immediately after addition of excess silver nitrate and nitric acid, in that silver chloride adsorbs silver ions. This error can easily be avoided by shaking the mixture for 5 minutes or longer, or by boiling for a few minutes, to coagulate the silver chloride before filtration. Excellent results can then be obtained by the filtration method; practically all the adsorbed silver returns to solution during the aging of the precipitate.

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[44] M. A. Rosanoff and A. E. Hill, *J. Am. Chem. Soc.*, **29**, 269 (1907). I. M. Kolthoff, *Z. anal. Chem.*, **56**, 568 (1917).

[45] J. Volhard, *Ann.*, **190**, 24 (1878).

Rothmund and Burgstaller[46] proposed that the aqueous solution be covered with ether, isobutyl alcohol, amyl alcohol, or some other immiscible organic liquid. The silver chloride agglomerates at the interface and is in effect withdrawn from the action of the thiocyanate solution. When applied to very dilute solutions, this method is preferable to the original Volhard procedure without filtration, but still the results may not be entirely accurate. In the presence of ether a small amount of silver disappears from solution because of occlusion in the precipitate. Depending on the conditions under which the end-point is determined, an error as large as 0.6% may be introduced.

Shchigol[47] reports that accurate results can be obtained by using benzene, toluene, or xylene in place of ether. From 5 to 10 ml. of the organic liquid is added to the halide solution, then an excess of silver nitrate is introduced, along with some nitric acid, and the solution is shaken. The silver chloride collects at the interface, leaving the aqueous and organic layers clear. Ferric solution is added as indicator and the back-titration is made with thiocyanate. The color at the end-point remains for some time.

Caldwell and Moyer[48] suggested the use of nitrobenzene as an immiscible liquid to protect the precipitate. Their procedure has been found quite useful. The nitrobenzene lowers the rate of solution of silver chloride and thereby its rate of reaction with thiocyanate.

Procedure: Prepare the solution so that 0.05–0.25 g. of alkali chloride is present in a volume of 25–50 ml., with 2–4 ml. of 6 N nitric acid. Add 1 ml. of nitrobenzene per 0.05 g. of chloride, then introduce an excess of 0.1 N silver nitrate. Stopper the flask and shake vigorously for half a minute or more, until the precipitate separates out in white curds. Add 1 ml. of ferric alum indicator solution and titrate with 0.1 N thiocyanate to a permanent red-brown color. One drop before the end-point a color is obtained which disappears upon shaking.

Note: Caldwell and Moyer obtained results accurate to within 0.2% on the specified quantities of sodium chloride. There is, however, a slight error which can usually be compensated by standardization of the solutions in the same way but which is significant in the titration of smaller quantities of chloride such as impurities in commercial salts.

The thiocyanate titration should be performed at a temperature of not more than 25°C., a requirement which is common to most modifications of the Volhard method.

It has been found by McKittrick and Schmidt[49] that accurate results can be obtained without filtration if the solution being titrated contains from

[46] B. Rothmund and A. Burgstaller, *Z. anorg. Chem.*, **63**, 330 (1909).

[47] M. B. Shchigol, *Z. anal. Chem.*, **91**, 182 (1932).

[48] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[49] D. S. McKittrick and C. L. A. Schmidt, *Arch. Biochem.*, **6**, 273 (1945).

40 to 65% of acetic acid. Apparently the solubility of silver chloride becomes lower than that of silver thiocyanate in this medium; no fading of the end-point occurs within 24 hours. Chloroform may be added to aid in coagulating the precipitate. The procedure followed by McKittrick and Schmidt was designed particularly for small quantities of chloride.

Procedure: To about 4 mg. of chloride in 10 ml. of water in a glass-stoppered test tube (1 × 8 inch) add 1 ml. of nitric acid, 15 ml. of chloroform and 20 ml. of acetic acid, or enough to make its concentration in the aqueous phase 40–65% by volume at the end-point. From a burette or pipette introduce 10 ml. of 0.02 N silver nitrate (an excess of about 5 ml.) and shake violently for one minute to coagulate the silver nitrate. Add 0.5 ml. of saturated ferric alum solution and titrate with 0.02 N potassium thiocyanate, shaking vigorously between additions, until there is obtained a color change which is permanent even after prolonged shaking. Standardize the thiocyanate solution against the silver nitrate under similar conditions, but in the absence of chloride. The end-points of samples and standards should be adjusted to the same color when viewed through the depth of the tubes, for greatest accuracy.

Interfering Substances in Volhard Titrations: Compounds which have a strong oxidizing action interfere by reacting with thiocyanate. They should be reduced beforehand by treatment with ferrous sulfate or a similar reducing agent. The lower oxides of nitrogen also attack thiocyanate and should be expelled before back-titration.

According to Berry[50] the interference of thallic ions can be eliminated by passing the solution through a Jones reductor loaded with zinc amalgam (2%). In place of using the Volhard method, Berry places the reduced solution in a burette and titrates a known quantity of silver nitrate with it, using tartrazine as an adsorption indicator (see p. 296).

Salts of mercury and palladium interfere by reacting with thiocyanate. They may be removed by precipitation with hydrogen sulfide before the addition of silver nitrate. The excess of sulfide is easily removed by gentle boiling of the acid solution for a few minutes[51]; sulfite can be eliminated in the same way. If much

[50] A. J. Berry, *Analyst*, **61**, 315 (1936).

[51] P. Khadanov, *Chimie & industrie*, **31**, 416 (1934). M. M. Maglio and F. Fazio, *Ind. Eng. Chem., Anal. Ed.*, **15**, 265 (1943), reported good results in using this method on synthetic mixtures of sodium bisulfide and sodium chloride but found that mercaptans cause interference. Therefore they precipitate the sulfur compounds with an excess of 5% cupric nitrate trihydrate solution at a p_H of 4, allow to stand for 15 minutes, filter, and determine chloride in the filtrate.

sulfite is present in solution the silver chloride precipitate is likely to contain a little too much silver, even though silver sulfite is soluble in dilute nitric acid.

Cyanide is also precipitated by silver nitrate. It is usually determined separately by the Liebig-Denigès method (p. 282) and a correction for it is applied to the result of the Volhard titration. See, however, pp. 266–268.

The Volhard method applied directly to a mixture of halides can determine only the total halide content. Preliminary treatment is necessary for the determination of chloride alone in a mixture. Some methods which have been found useful are described in the following paragraphs.

Chloride in the Presence of Bromide or Iodide: Various methods have been proposed for oxidizing bromide and iodide to the free halogens and expelling them by boiling. Bugarszky[52] proposed the use of iodate, which under suitable conditions of acidity furnishes the appropriate oxidation potential. Andrews[53] improved the method and applied it to the determination of chloride in commercial bromides.

Procedure: Place the sample, calculated to contain 10–50 mg. of chloride, in a Kjeldahl flask with a capacity of 400–500 ml. and a neck 20–25 cm. long. Make an initial addition of 6 ml. of 0.2 N potassium iodate and 17 ml. of 2 N nitric acid, then for each gram of bromine (or 1.6 g. of iodine) expected add 75 ml. of the iodate solution and 7.5 ml. of the nitric acid. Dilute to 200 or 250 ml. with water. Set the flask so that the bottom protrudes through a hole in an asbestos sheet or board, and heat with a burner until the liquid evaporates to about 90 ml. as shown by a mark previously made on the flask. Add 100 ml. of water and evaporate again to not less than 90 ml., repeating the process until no more halogen is detectable upon testing the vapor with starch-iodide or fluorescein paper. While still hot add 1 to 1.5 ml. of 25% phosphorous acid, boil until no iodine can be seen and then boil 5 minutes longer, keeping the volume above 90 ml. Cool and titrate the chloride by the Volhard method.

Note: Although the foregoing procedure is rather time-consuming, the authors regard iodate as one of the best oxidants for bromide and iodide. It causes no losses of chloride under the recommended conditions, even though used in excess, and the oxidation of the other halides is complete. When the Volhard method is used for the final titration, the excess of iodate must be removed since it causes a slight interference. The phosphorous acid reduction step is unnecessary, however, if the titration procedure of Lang and Messinger (p. 258) is employed, or if the chloride is determined mercurimetrically (p. 331).

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[52] S. Bugarszky, *Z. anorg. Chem.*, **10**, 387 (1895). For oxidation with a mixture of manganese dioxide and manganese sulfate, see I. E. Orlow, *Z. anal. Chem.*, **84**, 185 (1931).

[53] L. W. Andrews, *J. Am. Chem. Soc.*, **29**, 275 (1907).

Strong oxidants such as bromate, if present in excess of the bromide and iodide, must be reduced before the Andrews method is applied; otherwise some of the chloride will be oxidized.

Berg[54] developed a procedure in which bromine and iodine are allowed to react with acetone instead of being expelled by boiling. Bromate in strongly acid solution is used as oxidant for the halides other than chloride. Assuming that monosubstitution products of the acetone are formed, the following equations represent the reactions involved:

$$HBrO_3 + 2HI + 3C_3H_6O \rightarrow 2C_3H_5OI + C_3H_5OBr + 3H_2O$$
$$HBrO_3 + 2HBr + 3C_3H_6O \rightarrow 3C_3H_5OBr + 3H_2O$$

Bromate is added to the mixture until no more yellow color appears and again disappears with each addition, showing that the bromide and iodide have been consumed. No suitable indicator for the completion of this oxidation could be found. In view of the fact that the end-point is difficult to recognize, a small excess of bromate must be added to assure quantitative oxidation.

Procedure: To 50–60 ml. of halide solution are added 20–30 ml. of acetone and sufficient sulfuric acid to make a concentration of 1–1.5 N at the end of the oxidation. The solution is next treated with an 0.8% potassium bromate solution. The iodine is liberated first (detectable by a strong and finally a slight starch–iodine color) and then the bromine, both uniting with the acetone. In the oxidation of bromide, the bromate addition must be regulated so that the solution maintains a yellow color. After the disappearance of this color an excess of 3–5 ml. of bromate solution is quickly added. The solution must now remain colorless.

The excess bromate is destroyed immediately by adding dropwise (at the rate of one drop per second) an excess of 5% ferrous salt solution, with thorough shaking. The chloride is titrated by the Volhard method after the addition of 2 N nitric acid and several milliliters of ferric alum solution.

Using this method the chloride in various commercial products of bromide and iodide can be determined. The authors do not consider that the procedure is as suitable for traces of chloride as the Andrews method, however.

McAlpine[55] modified Berg's method and recommended the use of permanganate instead of bromate as oxidant.

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[54] R. Berg, *Z. anal. Chem.*, **69**, 342 (1926).

[55] R. K. McAlpine, *J. Am. Chem. Soc.*, **51**, 1065 (1929).

Procedure: To 10 ml. of halide solution are added 25 ml. of acetone and 50 ml. of 1.5 N sulfuric acid. Then a 5% potassium permanganate solution (chloride-free) is introduced dropwise until the pink color does not disappear, plus an excess of 15–20 drops. After 2 minutes, 2 ml. of 3% hydrogen peroxide is added. McAlpine determined the chloride in the solution gravimetrically; it can also be titrated by the Volhard method.

If chloride is to be determined in the presence of rather large quantities of bromide, it is advisable to work at a somewhat greater acidity. The oxidation of hydrochloric acid is prevented by the addition of a manganous salt.

Procedure: 25 ml. of acetone, 10 ml. of 0.3 N manganous sulfate, and 50 ml. of sulfuric acid (1:1) are added to the bromide solution, and after cooling to 15–20°C., the mixture is titrated with a 5% permanganate solution until the color no longer disappears. Sufficient sulfuric acid is then introduced to make the concentration 11–11.5 N. The solution is again cooled and an excess of one drop of permanganate is added. After 90 to 120 seconds the permanganate is reduced with an excess of hydrogen peroxide, after which the chloride may be determined either gravimetrically or by argentometric titration. The error in determining from 1 to 200 mg. of chloride in the presence of 1 g. of potassium bromide amounts to ±1 mg.

McAlpine has also suggested a further modification for the determination of traces of chloride in the presence of still larger amounts of bromide.

Procedure: To 10 g. of bromide, in a 500 ml. Erlenmeyer flask, is added 0.1 g. less than the theoretical quantity of permanganate. 40 ml. of water and 20 ml. of 3 N manganous sulfate are then introduced. After the reagents have dissolved, 25 ml. of sulfuric acid (1:1) is added and the solution is heated until only enough bromine remains to give a light yellow color (30 to 50 minutes). The following oxidation takes place:

$$2KMnO_4 + 10KBr + 8H_2SO_4 \rightarrow 5Br_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O$$

After the solution has cooled, 10 ml. of acetone and sufficient sulfuric acid to make the solution 11–11.5 N are added. The solution is again cooled and 5% potassium permanganate is added dropwise until a pink color appears. Several drops are taken in excess and approximately 2 minutes are allowed for the complete absorption of bromine. The determination is continued from this point according to the above procedure.

Lang and Messinger[56] modified Andrews' method of oxidation with iodate, titrating the chloride with silver nitrate using diphenylamine blue as adsorption indicator. The excess of iodate does not have to be removed before the titration.

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[56] R. Lang and J. Messinger, *Z. anal. Chem.*, **88**, 336 (1932).

Procedure: A 25 ml. sample of the neutral halide solution, not over about 0.2 N in chloride and 0.1 N in bromide, is placed in an Erlenmeyer flask along with 5 ml. of 85% phosphoric acid and 0.2–0.3 g. of potassium iodate. The mixture is diluted to 40 ml. and heated until all of the bromine has been evolved as evidenced by complete disappearance of the yellow color. During heating the volume should not be allowed to drop below 30 ml. or some chloride may be lost; it should be kept close to 40 ml. The colorless solution is heated for 10 minutes longer and is cooled, then after the addition of freshly prepared diphenylamine blue indicator it is titrated with 0.1 N silver nitrate (see p. 258).

Note: The procedure as given above is said to be inapplicable in the presence of iodide because some chloride is oxidized by hypoiodous acid formed intermediately during the reaction between iodate and iodide in strongly acid solution. The difficulty is avoided by first expelling iodine from the solution after addition of 10–20 ml. of acetic acid and 0.3 g. of potassium iodate; without cooling the mixture, 5 ml. of phosphoric acid is then added and the procedure is continued as before.

Lang and Messinger also used Berg's acetone method for eliminating bromide or iodide and obtained good results in titrating the remaining chloride by their diphenylamine blue procedure. They tested only mixtures in which the halides were present in concentrations of similar magnitude; further tests should be made before the method is applied to the determination of traces.

Halides in the Presence of Cyanide or Thiocyanate: Cyanide reacts reversibly with formaldehyde to form a cyanohydrin, hydroxyacetonitrile, which exists as an anion in alkaline solution:

$$CN^- + HCOH \rightleftarrows CNCH_2O^-$$

An excess of either reactant shifts the equilibrium to the right. According to Lippich[57] a slight excess of cyanide serves to remove all the formaldehyde; Votoček and Kotrba[58] recommend that a fivefold excess of formaldehyde be used for binding cyanide. The following procedure for determining halides or thiocyanate in the presence of cyanide is described by Schulek.[59]

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[57] F. Lippich, *Z. anal. Chem.*, **76**, 241 (1929). Lippich used the reaction for an argentometric determination of formaldehyde. See also G. Romijn, *ibid.*, **36**, 18 (1897).

[58] E. Votoček and J. Kotrba, *Collection Czechoslov. Chem. Commun.*, **1**, 165 (1929).

[59] E. Schulek, *Z. anal. Chem.*, **65**, 433 (1924). *Cf.* K. Polstorff and H. Meyer, *ibid.*, **51**, 601 (1912).

Procedure: From 0.1 to 0.3 g. of the mixed salts are dissolved in 50 ml. of water in a 150 ml. flask and treated with 5 ml. of 20% formaldehyde. The solution is shaken thoroughly, 5 ml. of about 6 N nitric acid is added and an excess of 0.05 N silver nitrate is measured in. After filtration the excess silver in the filtrate is determined by the Volhard method. Schulek reports results accurate to within about 0.1 mg. in the determination of 2–17 mg. of chloride, 4–40 mg. of bromide, or 3–30 mg. of thiocyanate, in the presence of 0.1 g. or more of cyanide.

Note: The reaction of cyanide with formaldehyde was studied further by Mutschin,[60] who found a threefold excess of aldehyde sufficient to prevent interference with an argentometric titration. The equilibrium is reached rapidly in alkaline solution but more slowly in the presence of acid; no appreciable hydrolysis of the nitrile occurs during a five minute titration period. Mutschin makes the sample slightly alkaline and treats with excess formaldehyde (2–3 ml. of 35% solution per 40 ml. of 0.1 N cyanide, or enough to remove the cyanide odor). He then neutralizes to neutral red with dilute nitric acid and titrates chloride or bromide by Mohr's method. Apparently it would be more convenient to carry out both the reaction and titration in a bicarbonate or borax solution.

Mutschin also titrated with the aid of adsorption indicators, using eosin for the determination of bromide, iodide, or thiocyanate in the presence of a little acetic acid. Starch-iodide indicator (p. 274) could also be used satisfactorily for the titration of iodide.

Schulek[59] gave an alternative method of eliminating cyanide, in which the neutral solution is treated with a little coarse pumice and a gram of boric acid, then is boiled for 10 minutes to drive out the liberated hydrocyanic acid. After cooling, the halides are determined by Volhard's method. Schulek states that the results are a little high, probably because of incomplete removal of cyanide. A similar procedure is given by Berry,[61] who uses potassium bitartrate in place of boric acid and titrates the remaining halides with an adsorption indicator. He gives methods for analyzing mixtures of chloride, iodide, and cyanide.

Cyanide and thiocyanate are oxidized by hydrogen peroxide in strongly alkaline solution as shown in the following equations:

$$KCN + KOH + H_2O_2 \rightarrow K_2CO_3 + NH_3$$

$$KCNS + 3KOH + 4H_2O_2 \rightarrow K_2CO_3 + K_2SO_4 + NH_3 + 4H_2O$$

According to Schulek[62] the oxidation of thiocyanate proceeds to the extent of about 98% of the theoretical (as indicated by the equation) and a little nitrite is formed by a side reaction. Under the same conditions cyanate is easily hydrolyzed:

$$KCNO + KOH + H_2O \rightarrow K_2CO_3 + NH_3$$

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[60] A. Mutschin, *Z. anal. Chem.*, **99**, 335 (1934).

[61] A. J. Berry, *Analyst*, **61**, 315 (1936).

[62] E. Schulek, *Z. anal. Chem.*, **112**, 415 (1938).

Schulek makes use of these reactions for the determination of chloride or bromide in mixtures with the cyano compounds. Iodide interferes by catalyzing the decomposition of hydrogen peroxide.

Procedure: The sample, containing up to 0.5 g. of alkali cyanide with 5–160 mg. of bromide or 3–70 mg. of chloride, is placed in a 200 ml. Erlenmeyer flask and dissolved in 50 ml. of water. 10 ml. of 10% sodium hydroxide and 5 ml. of halogen-free 30% hydrogen peroxide are added and the mixture is boiled for 10 minutes, carefully, with the flask in an inclined position. After cooling, 25 ml. of 10% nitric acid is added and the halides are titrated by the Volhard method.

In case thiocyanate is also present, one uses 10 ml. of hydrogen peroxide and boils for 15 minutes. The solution is cooled, 5 ml. more of peroxide is added and boiling is continued for 10 minutes longer. The determination is completed as before.

Cohen and Piepenbroek[63] studied various methods for eliminating thiocyanate and recommended oxidation with strong hydrogen peroxide in acid solution.

Procedure: To a solution which is 0.1 N or less with respect to chloride and thiocyanate add 1 ml. of 4 N sulfuric acid, 15 ml. of perhydrol, and water to make a total volume of 60 ml. Place a funnel or trap in the neck of the flask and quickly heat the contents to boiling, then keep just at the boiling point for 15 minutes. Cool the solution and determine chloride by the Volhard method. Larger amounts of sulfuric acid should be avoided since they may cause losses of chloride during the boiling and are also somewhat objectionable in the Volhard titration.

For the determination of traces of chloride in thiocyanates see the purity tests for potassium thiocyanate, p. 253.

Determination of Chlorine in Organic Compounds: The halogen of an organic compound must be converted into inorganic form before it can be determined by the common volumetric or gravimetric methods. Several ways of bringing about the conversion have been described.[64] One of the most practical methods for general use consists in decomposing the organic material with sodium peroxide in a Parr peroxide bomb.[65] As a bomb one may employ a heavy mild steel cup of 20 to 25 ml. capacity, having a lead-gasketed cover which provides an effective seal when the threaded coupling that holds it in place is tightened with a wrench.

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[63] E. Cohen and K. Piepenbroek, *Z. anal. Chem.*, **99**, 258 (1934).

[64] Decomposition with nitric acid in a sealed tube: L. Carius, *Ann.*, **116**, 1 (1860); **136**, 129 (1865); *Ber.*, **3**, 697 (1870). Reaction with sodium in alcohol or other solvent: A. Stepanov, *Ber.*, **39**, 4056 (1906); Q. Landis and H. J. Wichmann, *Ind. Eng. Chem., Anal. Ed.*, **2**, 394 (1930). Reaction with sodium in liquid ammonia: F. B. Dains and R. Q. Brewster, *J. Am. Chem. Soc.*, **42**, 1573 (1920). Oxidation with fuming sulfuric acid and other oxidants: J. J. Thompson and U. O. Oakdale, *J. Am. Chem. Soc.*, **52**, 1195 (1930); *ibid.*, **55**, 1292 (1933);

Procedure: The charge in the bomb is made up of 15 g. of reagent grade sodium peroxide, not more than about 0.5 g. of the sample, calculated to contain up to 0.1 g. of chlorine, and enough sugar so that the sum of the sugar and organic matter from the sample is about 0.8 g. Liquid samples of low volatility and which do not attack gelatin are best weighed out in gelatin capsules; other liquids are sealed in small glass bulbs. A solid sample may be placed in a gelatin capsule which is emptied into the peroxide and included with the charge just before sealing the bomb, or it may be mixed with the charge on a piece of glazed paper in a dry atmosphere. In loading the bomb, a 2 mm. layer of peroxide is first placed on the bottom, then the peroxide–sugar mixture and sample are inserted and any particles remaining on the edge of the bomb are brushed in. The cover is sealed on tightly and, in the case of a solid sample, the bomb is shaken to mix the contents.

The bomb is placed in an appropriate shield (to protect the analyst against a possible explosion) and is heated from the side, well below the lead gasket, with a moderate flame from a blast lamp. Generally the ignition of the charge is indicated by the entire lower part of the bomb becoming a dull red. The bomb is then allowed to cool and is opened, and the cover is rinsed into a 400 ml. beaker with about 50 ml. of water. Any free carbon at the top of the cup is cautiously removed with a dry spatula and is also added to the beaker, then the cup is placed upright in the water. A watch glass is held ready to place over the beaker, the cup is gently tipped over with a glass rod or pair of crucible tongs, and the beaker is covered at once. After the vigorous reaction, which may have to be started by warming slightly, the cup is removed with tongs or rod and is rinsed thoroughly into the beaker.

To the strongly alkaline solution enough 1:1 nitric acid is added, gradually

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H. H. Willard and J. J. Thompson, *ibid.*, **52**, 1893 (1930) (micro method). Hydrolysis with ethanolamine, with or without sodium: W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296, 503 (1937). Combustion with calcium hydroxide: R. H. Kimball and L. E. Lufts, *ibid.*, **10**, 530 (1938).

[65] S. W. Parr, *J. Am. Chem. Soc.*, **30**, 764 (1908). See also H. H. Pringsheim, *Am. Chem. J.*, **31**, 386 (1904); J. F. Lemp and H. J. Broderson, *J. Am. Chem. Soc.*, **39**, 2069 (1917). The procedure given here is adapted from these. Micro modifications have been made by A. Elek and D. W. Hill, *J. Am. Chem. Soc.*, **55**, 2550 (1933), and by F. E. Beamish, *Ind. Eng. Chem., Anal. Ed.*, **5**, 348 (1933).

and with stirring, to neutralize most but not quite all of the alkalinity, and the mixture is filtered to remove iron oxide. If the acid has been added carefully, there should be practically no formation of ferric hydrous oxide which might adsorb some chloride. The clear solution is then acidified with nitric acid and the halide is determined by the Volhard method. The mixture containing excess silver nitrate may be concentrated by boiling before the silver chloride is filtered off, in order that the final volume may be small. Hydrogen peroxide is expelled at the same time.

Note: Optionally the alkaline solution may be made slightly acid and treated with excess silver nitrate before the filtration. This procedure brings more iron into solution.

If iodine is being determined, a reducing agent such as hydrazine sulfate should be added before the neutralization, to reduce iodate and prevent losses of free iodine.

Since sodium peroxide ordinarily contains a little chloride, a blank should be carried through the entire procedure.

Indirect Determination of Fluoride as Lead Chlorofluoride: Starck[66] developed a method for fluorine in which it is precipitated as lead chlorofluoride and weighed. He mentioned that one might also determine chloride in the precipitate, either gravimetrically or by the Volhard titration, and thus find the fluoride indirectly. Hawley[67] confirmed the applicability of the titration method and studied the most suitable conditions. Lead chlorofluoride is appreciably soluble in water but the solubility is diminished greatly by the presence of lead chloride. The procedure described below is that of Hoffman and Lundell,[68] who applied it for the analysis of glasses and enamels after fusing with an alkali carbonate and removing silica and other interfering substances with zinc oxide.

Lead Chlorofluoride Wash Solution: (*a*) Dissolve 10 g. of lead nitrate in 200 ml. of water; (*b*) dissolve 1.0 g. of sodium fluoride in 100 ml. of water and add 2 ml. of concentrated hydrochloric acid. Mix solutions (*a*) and (*b*), allow the precipitate to settle and decant the supernatant liquid. Wash four or five times with 200 ml. of water by decantation, add one liter of cold water to the precipitate and allow to stand for an hour or longer with occasional stirring. Filter and use the clear filtrate, reserving the precipitate for the preparation of more solution as needed.

Procedure: To a solution containing from 0.01 to 0.10 g. of fluorine add 2 drops of 0.4% bromophenol blue indicator and 3 ml. of 10% sodium chloride solution. Bring to a volume of about 250 ml. and adjust with dilute nitric acid and dilute sodium hydroxide just to a blue color. Add 2 ml. of 1:1 hydrochloric acid and 5.0 g. of solid lead nitrate, $Pb(NO_3)_2$. Heat on the steam bath and after the lead nitrate has dissolved add 5.0 g. of sodium acetate trihydrate. Stir vigorously and digest on the bath for half an hour with occasional stirring. Allow to stand for at least 4 hours, preferably overnight, at room temperature and decant through retentive paper. Wash the precipitate, beaker, and paper once with cold water, four or five times with saturated lead chlorofluoride wash solution and finally once more with cold water. Discard the filtrate.

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[66] G. Starck, *Z. anorg. Chem.*, **70**, 173 (1911). See also W. H. Adolf, *J. Am. Chem. Soc.*, **37**, 2500 (1915).

[67] F. G. Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

[68] J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, **3**, 589 (1929). *Cf.* F. Specht, *Z. anorg. allgem. Chem.*, **231**, 181 (1937).

Transfer precipitate and paper to the original beaker, stir up with 100 ml. of dilute nitric acid (5:95) and heat on the steam bath until the precipitate is dissolved. Determine chloride in the mixture by the Volhard method. Since equimolar quantities of chlorine and fluorine are present in the precipitate, each milliliter of 0.1 N silver nitrate is equivalent to 1.90 mg. of fluorine.

Notes: (1) With more than 0.10 g. of fluorine present, slightly high results are obtained. Results are a little low when somewhat less than 0.01 g. of fluorine is present and the method fails for very small amounts.

(2) To determine fluorine in phosphate rocks, Hoffman and Lundell[69] include a preliminary distillation as hydrofluosilicic acid (*cf.* p. 324).

(3) Fluorine in organic compounds may be brought into inorganic form by decomposition with sodium in an evacuated tube, according to Elving and Ligett.[70]

DETERMINATION OF BROMIDE

(*a*) ***Mohr Method:*** Bromide may be determined conveniently by the Mohr method (p. 242). The considerations presented in connection with the determination of chloride apply as well to the titration of bromide.

(*b*) ***Fajans Method:*** The applications of fluorescein, dichlorofluorescein, eosin, and several other compounds as adsorption indicators in bromide titrations have been mentioned on pp. 245–250. Eosin is an excellent indicator which may be used even with very dilute solutions. The titration is best carried out in a medium slightly acidified with acetic acid (about 0.1 N). 1 to 3 drops of a 0.5% solution of the sodium salt of eosin are taken for 10 ml. of 0.1 N bromide solution, or for 25 ml. of a weaker solution, and the titration is made with silver nitrate solution of appropriate strength.

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[69] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards,* **20,** 610 (1938).

[70] P. J. Elving and W. B. Ligett, *Ind. Eng. Chem., Anal. Ed.,* **14,** 449 (1942).

Early in the titration silver bromide begins to flocculate; the precipitate may be colored slightly by the indicator but does not become intensely red until the equivalence-point is reached. High concentrations of electrolytes, especially of multivalent cations, may interfere.

Kolthoff attempted to determine bromide in the presence of chloride by titrating in the presence of ammonium carbonate, but without success. The end-point comes too late and is not sharp. Apparently in the alkaline solution eosin ions are partially displaced from the surface of the precipitate by hydroxyl ions.

(*c*) ***Volhard Method:*** The Volhard titration of bromide gives very good results. Silver bromide does not react appreciably with thiocyanate ions and therefore need not be removed before the back-titration of excess silver nitrate. Thiocyanate is added until a pale red-brown color of ferric thiocyanate persists after vigorous shaking. The indicator solution and proper conditions of acidity are described on page 250. A simplification of the method, in which the only standard solution needed is silver nitrate, has been proposed by Kolthoff.[71]

Procedure: To 10 ml. of bromide solution add 1 ml. of ferric ammonium sulfate solution, 10 ml. of 4 N nitric acid, and 0.1 to 0.2 ml. of approximately 0.1 N thiocyanate. Titrate with standard silver nitrate to the disappearance of the red-brown color. Titrate also a blank with the same quantity of indicator and other reagents and subtract this from the volume of silver nitrate required by the sample.

Notes: (1) The ratio of the solubility product of silver bromide to that of silver thiocyanate is about 0.5. From this it may be deduced that the color of the indicator is removed shortly before the equivalence-point and that the titration error is small.

(2) The method is well suited for the rapid analysis of commercial salts which may contain some chloride. If the titration is continued until the red-brown color definitely fades but is still pale rose, the bromide may be determined to within 1% in the presence of as much as 5% of chloride (based on the total halogen content). In the presence of chloride the solution should not be titrated until colorless since a major portion of the chloride would then be included.[71] For more accurate work it is preferable to determine the total halogen content argentometrically, then expel bromine from another sample by the method of Andrews or McAlpine, and determine the chloride directly. Bromide is then calculated by difference; iodide is generally absent from the commercial bromides manufactured in this country.

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[71] I. M. Kolthoff, *Pharm. Weekblad*, **54**, 761 (1917).

DETERMINATION OF IODIDE

(*a*) ***Mohr Method:*** Iodide cannot be determined accurately by the Mohr method, because the color change is unsatisfactory.

(*b*) ***Fajans Method:*** Good results may be obtained using fluorescein, dichlorofluorescein, or eosin as indicator; these are discussed on pages 245, 247 and 248. Eosin is especially to be recommended, since with it accurate titrations may be performed even when the iodide solutions are very dilute.

Kocsis[72] makes use of the dyes Diamine Fast Bordeaux 6BS and Diamine Fast Violet BBN (British Colour Index No. 325) as adsorption indicators for the titration of iodide. The indicator solutions are made up to contain 0.1 g. per 100 ml. and are filtered if necessary. Either compound gives a red-violet color in an iodide solution, changing to yellow-green near the equivalence-point. After the equivalence-point has been reached, the precipitated silver iodide adsorbs the dye quite strongly. The reverse titration, of silver solution with iodide, is not satisfactory; neither is the argentometric titration of chloride or of bromide successful, for the color change is not distinct. In weakly acid solution only the Diamine Fast Violet may be employed as indicator for the titration of iodide and the p_H should not be lower than 2.7 in this case. The same indicator serves for the determination of iodide in the presence of chloride (p. 277).

(*c*) ***Volhard Method:*** The Volhard titration is capable of giving excellent results for iodide. Ferric alum indicator solution should not be added until the iodide has been precipitated with an excess of silver; otherwise some oxidation to free iodine is likely to take place.

(*d*) ***Clear-Point Method:*** Iodide solutions not stronger than about 0.04 N may be titrated directly to a clear-point with silver nitrate. The silver iodide begins to flocculate about 1% before the equivalence-point and the titration is continued dropwise, with vigorous shaking after each addition, until the supernatant liquid becomes perfectly clear. Excellent results are obtained in the absence of foreign electrolytes.[73]

(*e*) ***Starch–Iodide Method:*** Starch and iodine may be used to indicate the end-point when iodide is titrated with silver nitrate. An aqueous solution of iodine is partly hydrolyzed:

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[72] E. J. Kocsis, *Z. anorg. allgem. Chem.*, **221**, 318 (1935).

[73] The precision of this titration has been investigated by W. Ponndorf, *Z. anal. Chem.*, **84**, 331 (1931).

[74] I. M. Kolthoff, *Pharm. Weekblad*, **54**, 763 (1917); **58**, 917 (1921). F. Pisani, *Compt. rend.*, **43**, 1118 (1856); *Ann. mines*, **10**, 83 (1856). L. W. Andrews,

$$3I_2 + 3H_2O \rightleftarrows IO_3^- + 5I^- + 6H^+$$

$$K = \frac{[H^+]^6\,[I^-]^5\,[IO_3^-]}{[I_2]^3}$$

The equilibrium constant varies greatly with the temperature but is always extremely small,[75] 3.8×10^{-49} at 18°C. and 5.1×10^{-42} at 60°. In other words, the equilibrium so strongly favors the formation of free iodine that in slightly acid solution the hydrolysis of iodine cannot be detected analytically. The equilibrium may be shifted, however, by addition of a silver salt which removes the iodide ions as insoluble silver iodide.

The typical blue color observed when iodine is added to starch depends not only upon the presence of these substances, but requires also the presence of iodide ions. If the iodide is removed, the color fades. Therefore when a solution of iodide, containing a little starch and free iodine, is titrated with silver nitrate, the color disappears as soon as the iodide is all precipitated. Ponndorf[76] studied the titration and found that free iodine is still present in the solution at the end-point; Kolthoff[74] had already shown potentiometrically that iodate is also formed.

Procedure: The iodide solution, which should be neutral or slightly acid with sulfuric acid, is treated with 2 to 5 ml. of 0.2% starch solution and a drop of either 0.1 N potassium iodate or a very dilute alcoholic solution of iodine. The liquid should assume a distinct blue coloration. During titration with silver nitrate the color gradually fades to green, until as the end-point is approached the silver iodide coagulates and becomes green through adsorption of the indicator. The titration is continued slowly with vigorous shaking until the green color changes to yellow. Comparison with a sample that has already been titrated is helpful in judging the end-point, which ordinarily occurs 0.2 or 0.3% before the equivalence-point.

Am. Chem. J., **24**, 256 (1900). P. Fleury and J. Courtois, *Bull. soc. chim.*, [4], **49**, 860 (1931). S. Prikladovitzkii and A. Appollonov, *Biochem. Z.*, **200**, 135 (1928).

[75] E. Abel, *Nernst-Festschrift*, p. 1, Halle 1912; *Chem. Abstracts*, **7**, 927 (1913). R. Luther and V. Sammet, *Z. Elektrochem.*, **11**, 293 (1905). V. Sammet, *Z. physik. Chem.*, **53**, 641 (1905). R. Abegg, *Handbuch der anorganischen Chemie*, Vol. IV, Part 2, Hirzel, Leipzig 1913, p. 519.

[76] W. Ponndorf, *Z. anal. Chem.*, **85**, 5 (1931).

Notes: (1) The color change may be observed in the liquid rather than on the precipitate if sufficient starch is added to serve as a protective colloid (20 to 25 ml. of 0.2% starch to 25 ml. of solution) and if the solution is neutral.

(2) Solutions as dilute as 0.001 N may be titrated quite sharply in neutral or acid solution. The titration error amounts to nearly 0.5%, the end-point coming too soon.

(3) The method may be applied to the analysis of crude iodides or other mixtures in which the bromide content is less than 3%, or the chloride 20%, of the iodide content. Under these conditions the error in the iodide determination may amount to 1%. If more bromide or chloride is present, useful results may be obtained by adding ammonium carbonate to the solution (see p. 277).

(4) Ponndorf[76] applied his refined titration methods to the procedure and found it to be capable of accuracy within 0.03%. As indicator he uses a mixture of 20 ml. of water, 2 ml. of 0.002 N potassium iodide–iodine solution, 2 ml. of freshly prepared 1% starch solution, and 1 drop of 6 N sulfuric acid. This is titrated with 0.002 N silver nitrate to a yellow color, before addition to the sample. It then contains free iodine but no iodide.

(5) Chirnoagă[77] adds to the iodide solution a drop or two of saturated ferric sulfate and then 2 ml. of 0.4% starch, thus obtaining indicator action without the introduction of additional iodine. He reports good results for iodide alone in neutral or acid solution, though bromide and chloride interfere. The interference of chloride may be prevented by treating the sample with an equal volume of 2 M sodium acetate. Kolthoff's procedure may be used in the presence of bromide.

(*f*) ***Cinchonine–Bismuth Nitrate Method:*** A weakly acid solution of cinchonine and bismuth nitrate gives with iodide an orange precipitate, $C_{19}H_{22}N_2O \cdot HBiI_4$. Upon titration of the mixture with silver nitrate, uncombined iodide is precipitated first and then the iodide from the orange compound reacts. The end-point is reached when the color changes from a red-brown to a bright yellow.[78]

Indicator Solution: Dissolve 2.33 g. of bismuth oxide in 10 ml. of warm concentrated nitric acid and dilute with 20 ml. of water. Add 2.94 g. of cinchonine, dilute to 100 ml. with water, and remove any nitrous acid by adding 0.1 g. of urea.

Procedure: Adjust the acidity of the iodide solution by adding a few drops of 2,6-dinitrophenol indicator and just enough 2 N nitric acid to bring about disappearance of the yellow color. Use 0.5 to 1 ml. of the cinchonine–bismuth nitrate solution for 10 to 50 ml. of sample and titrate with standard silver nitrate until the red color fades and only the yellow silver iodide precipitate is present. With 0.1 N solutions the titration error is about 0.5% and the results are low because of the solubility of cinchonine–bismuth iodide.

Notes: (1) A distinct reaction with the indicator is obtained with 0.1 mg. of iodide in 1 ml. of water. The sensitivity is greatest at a p_H of 2.4 though the change is more distinct at 1.6. Using benzoylcinchonine the sensitivity is said to be increased fivefold.

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[77] E. Chirnoagă, *Z. anal. Chem.*, **102**, 339 (1935).

[78] R. Uzel, *Collection Czechoslov. Chem. Commun.*, **5**, 383 (1933).

(2) Because of the indicator solubility, the titration error increases considerably when more dilute solutions are analyzed. With 0.01 N solutions the error is about 5% and an indicator correction should be applied.

(3) Salts of mercury and iron interfere, but most other cations and anions do not. Phosphate and arsenate give a precipitate with bismuth and more indicator should be used in their presence.

(4) Iodide may be titrated in the presence of 20 times as much chloride (in equivalents) or 4 times as much bromide. With a larger proportion of bromide the titration is carried out in 50% isopropyl alcohol. The ratio of bromide to iodide may then be as great as 20:1. Neither cyanide nor small quantities of thiocyanate interfere if the titration is performed slowly in an acid medium. Ferrocyanide and cobalticyanide may be precipitated with a zinc salt; in the presence of nitroprusside the solution should be diluted and the end-point matched against a suspension of silver iodide containing nitroprusside.

IODIDE IN THE PRESENCE OF CHLORIDE OR BROMIDE

(*a*) ***Fajans Method:*** Iodide ions are much more strongly adsorbed on silver iodide than are chloride or bromide ions. If a solution of chloride and iodide is titrated, silver iodide alone is precipitated until the iodide concentration becomes only one one-millionth of the chloride concentration (see Vol. I, p. 39). In other words, practically all of the iodide must be precipitated before any silver chloride can be formed. If an adsorption indicator is added which is adsorbed more strongly by silver iodide than is chloride, but less strongly than iodide, the indicator should behave as follows: As long as unprecipitated iodide ions are present the dye anions also remain in solution, but as soon as the amount of silver added becomes equivalent to the iodide, adsorption of the dye occurs (with a consequent change in color) in spite of the presence of chloride.

Fajans and Wolff[79] pointed out that Rose Bengale, diiodofluorescein, and dimethyldiiodofluorescein are satisfactory indicators. The last, in which the substituent groups are all on the resorcinol ring, is especially suitable.

Indicator Solution: A 1% solution of the sodium salt in water is recommended. Approximately 1 ml. of indicator is used for 25 ml. of 0.1 N potassium iodide.

Procedure: The sample, diluted so that the iodide concentration is less than 0.02 N, is treated with indicator and titrated with silver nitrate until the color changes from orange-red to bluish red. The color change, which is not very sharp, passes first through a brownish red and then through a carmine-red tint before the end-point is reached. For exact work it is necessary to have a reference solution of about the same composition as the system being titrated. The color change occurs somewhat late in the presence of chloride, the error depending upon the relative quantities of chloride and iodide as shown in the accompanying table. With changes of sign the values given may be applied as corrections; they are valid for titrations of 100 to 200 ml. of 0.01 to 0.02 N potassium iodide.

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[79] K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, **137**, 230 (1924). K. Fajans and O. Hassel, *Z. Elektrochem.*, **29**, 495 (1923).

ERRORS IN TITRATING IODIDE IN THE PRESENCE OF CHLORIDE
(According to Fajans and Wolff)

$\frac{[KCl]}{[KI]}$	Error, %	$\frac{[KCl]}{[KI]}$	Error, %
0.00	−0.1	0.07	+0.95
0.01	+0.2	0.08–0.5	1.0
0.02	0.4	0.75	0.9
0.03	0.55	1.0	0.85
0.04	0.7	1.5	0.65
0.05	0.8	2.0	0.5
0.06	0.9	4.0	0.45

In a mixture of iodide and chloride the iodide is determined first, using dimethyldiiodofluorescein as indicator, then the sum of the two is found using fluorescein. The former titration yields an approximation of the iodide content which may be corrected on the basis of the chloride found by difference.

Kolthoff has attempted to titrate iodide in the presence of bromide in ammoniacal solution with the above indicators. Under these conditions the end-point of the iodide titration comes much too late. Hydroxyl ions apparently displace the dye ions from the surface of silver iodide. However, using eosin in ammonium carbonate solution, iodide may be determined accurately in the presence of large quantities of chloride.[80] For 100–200 ml. of solution one adds 5 ml. of 0.5 N ammonium carbonate and titrates until the color changes to a purple-violet. In this way the author was able to titrate 250 ml. of 0.001 N iodide, in the presence of 1 g. of potassium chloride, with an error of 1% or less.

Other indicators which have been suggested for titration of iodide in the presence of chloride are Brilliant Orsella C and Chromotrope F4C (see p. 249) or Diamine Fast Violet BBN (p. 273). The anions of these compounds are more strongly adsorbed by silver iodide than are chloride ions. Silver iodide remains in colloidal solution near the first equivalence-point and the suspension changes color at this point, generally from pink to green though the hues vary with the different indicators. Using Diamine Fast Violet, the color change from red-violet to yellow-green is unaffected by the presence of chloride.

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[80] **I. M. Kolthoff, *Z. anal. Chem.*, 70, 395 (1927).**

(*b*) ***Starch–Iodide Method:*** Equilibrium in the hydrolysis of iodine (see p. 274) depends largely upon the hydrogen-ion concentration. At higher p_H values the system starch–iodine–iodide becomes more sensitive to silver ion and it is therefore to be expected that in the presence of a weak alkali like ammonium carbonate there will be less interference from chloride or bromide than in neutral or acid solution. This has been confirmed experimentally.[81]

Procedure: To 25 ml. of about 0.1 N iodide solution are added one drop of 0.1 N iodate and several drops of 4 N sulfuric acid, whereupon iodine is liberated and the solution becomes pale yellow. Several milliliters of 0.2% starch solution and 5–10 ml. of 2 N ammonium carbonate are added and the iodide is titrated with 0.1 N silver nitrate. The liquid and the silver iodide precipitate become gray during the titration. Silver nitrate solution is allowed to run in slowly, with vigorous shaking, until the precipitate becomes pale yellow. The end-point may be observed with an accuracy of 0.1 ml. of 0.1 N solution. The color change occurs somewhat too soon, the titration error amounting to about −0.6%.

Notes: (1) The titration gives good results even in the presence of 1 g. of potassium bromide or 5 g. of sodium chloride. It is the only argentometric iodide determination (other than potentiometric) that may be carried out in the presence of large amounts of bromide and chloride.

(2) The method cannot be used for the titration of very dilute iodide solutions because the end-point comes too early. In the titration of 0.01 N iodide the error may reach 10%. The concentration of iodide should be at least 0.05 N.

DETERMINATION OF THIOCYANATE

(*a*) ***Mohr Method:*** The end-point is difficult to recognize and the titration does not give good results.

(*b*) ***Fajans Method:*** Useful results can be obtained with fluorescein, dichlorofluorescein, or eosin as indicator. Details are much the same as in the titration of chloride or bromide (see pp. 247, 271).

Akiyama and Yabe[82] titrate thiocyanate in weakly basic solution using sodium alizarin sulfonate, phenolphthalein, bromophenol blue, or diphenylcarbazide as indicator. The first is said to be most suitable.

(*c*) ***Volhard Method:*** The direct titration of thiocyanate with silver nitrate, using ferric alum as indicator, is not satisfactory.

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[81] I. M. Kolthoff, *Pharm. Weekblad*, **62**, 1310 (1925).

[82] T. Akiyama and S. Yabe, *J. Pharm. Soc. Japan*, **55**, 77 (1935); *Chem. Abstracts*, **31**, 6994 (1937).

During titration the precipitated silver thiocyanate occludes ferric thiocyanate and the end-point is difficult to recognize. It is better to add an excess of silver nitrate before introducing the indicator and to back-titrate with a standard thiocyanate solution; under these conditions the determination is quite accurate. Direct titrations of thiocyanate are possible with a standard mercuric salt solution and ferric indicator (p. 338).

Determination of Free Sulfur: Castiglioni[83] applied the thiocyanate titration to the determination of free sulfur. The sulfur is extracted with a solvent (acetone) and the extract is refluxed for half an hour with an excess of potassium cyanide. The solvent is evaporated on a steam bath and the residue is taken up in about 100 ml. of water and transferred to a 200 or 250 ml. volumetric flask. Then 10 ml. of 20% formaldehyde solution is added to react with the excess cyanide.[84] The solution is carefully shaken, acidified with 5 ml. of 30% nitric acid, and diluted to the mark with water. After mixing, an aliquot portion is treated with a ferric salt as indicator and is titrated with silver nitrate. It would be preferable to add an excess of silver nitrate and back-titrate with thiocyanate, or to titrate directly with mercuric nitrate solution.

Determination of Aniline: Spacu and Dima[85] precipitate aniline as $Cu(C_6H_5NH_2)_2(SCN)_2$ with potassium thiocyanate and cupric sulfate, and back-titrate the excess thiocyanate. To 40–50 ml. of aniline solution in a 100 ml. glass-stoppered volumetric flask are added an excess of 0.1 N thiocyanate solution and 3–5 ml. of 10% copper sulfate. The flask is shaken vigorously until the precipitate coagulates well, then the solution is diluted to the mark, mixed thoroughly, and filtered. The excess thiocyanate in an aliquot portion is back-titrated with silver nitrate in the presence of a ferric salt. The procedure is accurate to about 1% and apparently might be useful for the determination of aniline in the presence of phenol.

DETERMINATION OF SELENOCYANATE

Silver selenocyanate is very slightly soluble in water, its solubility product having about the same magnitude as that of silver iodide. The salt forms fairly stable suspensions but in the presence of excess silver ions it decomposes with formation of metallic silver. For this reason the Volhard method is not applicable.

According to Ripan[86] good results are obtained by titrating 0.005 to 0.1

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[83] A. Castiglioni, *Z. anal. Chem.*, **91**, 32 (1933).

[84] E. Schulek, *Z. anal. Chem.*, **65**, 433 (1924).

[85] G. Spacu and L. Dima, *Z. anal. Chem.*, **110**, 25 (1937).

[86] R. Ripan, *Z. anal. Chem.*, **94**, 335 (1933).

M solutions of selenocyanate directly with silver nitrate in neutral solution, using fluorescein as adsorption indicator. The more dilute solutions must be titrated very slowly with vigorous shaking, so that 12 to 15 minutes are required for a titration.

Spacu and Macarovici[87] recommend diphenylcarbazone as an indicator. Silver ions form a violet complex with the carbazone; part of the complex is adsorbed by the precipitate and the rest remains in solution but decomposes within a few minutes until the end-point has been reached, after which the violet color remains.

Procedure: From 0.1 to 0.2 g. of alkali selenocyanate is dissolved in 20–25 ml. of water, or better in 20–25 ml. of 20% potassium nitrate solution, to retard hydrolysis. After addition of 6–8 drops of 0.5% alcoholic diphenylcarbazone solution the mixture is titrated with 0.05 N silver nitrate, meanwhile being stirred well, until the appearance of a stable violet color.

DETERMINATION OF CYANATE

Cyanate in the absence of interfering substances is best determined by the Volhard method, adding an excess of silver nitrate and back-titrating the latter in the filtrate.

A direct titration using fluorescein as indicator has been described by Ripan-Tilici,[88] who mentions that cyanate may also be determined in mixtures with cyanide but gives no details of this application.

Procedure: About 25 ml. of 0.01 to 0.02 M alkali cyanate is cooled to 14–16°C. and treated with 4 or 5 drops of 0.2% fluorescein. Rather strong silver nitrate solution (0.8 to 1 N) is added from a microburette, the end-point being difficult to recognize if a more dilute solution is used. Because of the relatively small volume of reagent and the poor end-point, the error may exceed 1%.

DETERMINATION OF CYANIDE

(*a*) ***Mohr Method:*** Cyanide may be titrated directly with silver nitrate, using chromate as indicator, if the solution is first made alkaline with magnesium hydroxide to prevent hydrolysis.[89] The titration gives good results but has little practical importance since chloride and cyanate interfere. The more specific method of Liebig and Denigès (*d* below) is preferable.

(*b*) ***Fajans Method:*** Good results can be obtained with fluorescein or dichlorofluorescein as indicator, if the titration is performed in the presence of excess sodium bicarbonate. The end-point is not very sharp, however. Eosin is not useful for the titration of cyanide.

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[87] G. Spacu and C. G. Macarovici, *Z. anal. Chem.*, **105**, 408 (1936).

[88] R. Ripan-Tilici, *Z. anal. Chem.*, **102**, 32 (1935).

[89] H. C. Vielhaber, *Arch. Pharm.*, [3], **13**, 408 (1878).

Ripan-Tilici[90] makes use of diphenylcarbazone, which acts as a p_H indicator as well as an adsorption indicator. The alkali cyanide solution (p_H = 9 to 12) is treated with 4 or 5 drops of 0.3% alcoholic diphenylcarbazone, the mixture becoming red-brown. During titration with 0.5 to 0.1 N silver nitrate this color disappears and when the cyanide has been transformed into complex $Ag(CN)_2^-$ ions the solution becomes violet. As the titration is continued slightly soluble silver argentocyanide is formed, the precipitate flocculating and becoming blue at the second equivalence-point. The titration must be carried out slowly, with much shaking to redissolve any precipitate formed during the first stages of the operation.

A similar method using diphenylcarbazide had already been proposed by Wellings,[91] who carries the titration only to the first equivalence-point as shown by a change from red to violet. A 0.1% solution of the indicator in alcohol is used, several drops being taken. The end-point is reported to be clearly perceptible even with 0.002 N solutions.

Ryan and Culshaw[92] prefer *p*-dimethylaminobenzylidine rhodanine (0.02% solution in acetone) as indicator. In the absence of other heavy metals an excess of silver ions gives a red color with this compound. One adds 10 ml. of 10% sodium hydroxide and 3 drops of indicator to the cyanide solution and titrates with 0.1 N silver nitrate until the solution first becomes red.

(*c*) ***Volhard Method:*** Although the solubility products of silver argentocyanide and silver thiocyanate have the same order of magnitude, an excess of silver cannot be back-titrated in the presence of argentocyanide. Hydrocyanic acid is a very weak acid and therefore the solubility of its silver salt is markedly increased in acid solution.

Good results can be obtained by precipitating the cyanide with an excess of silver nitrate. The mixture is acidified with nitric acid, diluted to a definite volume, and filtered. An aliquot portion of the filtrate is titrated with standard thiocyanate solution, just as in the Volhard method for chloride, p. 259.

The Volhard method is used, for example, in the determination of free hydrocyanic acid in bitter almond water (*cf.* p. 339). A portion of the solution is acidified, treated with an excess of silver, filtered, and titrated as above. For determination of the total cyanide content, another portion is first made ammoniacal and then treated with a liberal excess of silver nitrate, acidified with nitric acid, etc. In alkaline solution an equilibrium is quickly established:

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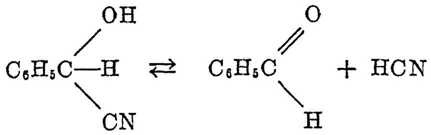
[90] R. Ripan-Tilici, *Z. anal. Chem.*, **118**, 305 (1939).

[91] A. W. Wellings, *Analyst*, **58**, 331 (1933).

[92] J. A. Ryan and G. W. Culshaw, *Analyst*, **69**, 370 (1944).



Since cyanide ions are removed by the silver solution the equilibrium is displaced to the right.

(*d*) ***Liebig-Denigès Method:*** This procedure is an example of a complex-formation method but for convenience it will be considered here. If silver nitrate is added to an aqueous solution of alkali cyanide, the complex argentocyanide ion is formed:

$$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^-$$

Only after all the cyanide has entered the complex can the slightly soluble silver argentocyanide (ordinarily called silver cyanide) be formed by a drop of silver nitrate in excess. The end-point is therefore detected by the first permanent turbidity. The theory of this titration has been discussed in Volume I, pp. 46, 69.

Liebig,[93] with whom the method originated, added sodium chloride to make the end-point more distinct; however, this addition is of no particular value.[94] The liquid may be made alkaline with sodium hydroxide to a concentration of 0.1 N, but not greater. Volhard[95] found that the turbidity may appear too early because the precipitate which is formed by local excesses of reagent dissolves only slowly in a slight excess of alkali cyanide. It is advisable to titrate with a dilute silver nitrate solution (0.02 N). Feldhaus[94] pointed out that ammonia interferes seriously by dissolving silver cyanide.

Denigès[96] introduced a great improvement by using potassium iodide as indicator and titrating in ammoniacal solution. The formation of slightly soluble silver iodide marks the end-point. The importance of having the

[93] J. Liebig, *Ann.*, **77**, 102 (1851).

[94] S. Feldhaus, *Z. anal. Chem.*, **3**, 34 (1864).

[95] J. Volhard, *Ann.*, **190**, 49 (1877).

[96] G. Denigès, *Compt. rend.*, **117**, 1078 (1893). *Cf.* H. Drehschmidt, *J. Gasbeleucht.*, **35**, 225 (1892); *Chem. Zentr.*, **1892**, I, 1007.

proper concentration of ammonia has not been stressed adequately in the literature. In a 0.1 N solution of potassium argentocyanide the concentration of silver ions is about 6×10^{-8} M. If the solution is at the same time 10^{-2} N in iodide ions, a precipitate of silver iodide will form since S_{AgI} is 10^{-16}. The turbidity thus appears too soon. In the presence of ammonia, however, the silver-ion concentration is reduced through formation of complex silver ammonia ions. With too little ammonia the end-point appears too soon and with a large excess of ammonia, too late. Denigès allows 1 or 2 ml. of 6 N ammonia and 0.2 g. of potassium iodide for 100 ml. of liquid. Kolthoff obtained somewhat better results by adding 5–8 ml. of 6 N ammonia. The titration with silver nitrate is made against a black background. The method gives excellent results in the analysis of alkali cyanides and of bitter almond water. In the latter case the total cyanide content is determined. 1 ml. of 0.1 N silver nitrate is equivalent to 5.4 mg. of hydrocyanic acid.

Notes: (1) It should be remembered that cyanide solutions are not stable. Ubbelohde[97] mentions that a 0.1 N solution of potassium cyanide loses strength at the rate of about 0.3% per day.

(2) Ubbelohde suggests the use of nickel dimethylglyoxime as indicator. As long as cyanide is present in excess the nickel is held as a cyanide complex and the solution remains colorless; when the cyanide has reacted with enough silver to form $KAg(CN)_2$, the pink color of the nickel oxime appears. The indicator mixture is prepared by diluting a 5% solution of potassium cyanide with an equal volume of alcohol and boiling with an excess of solid nickel dimethylglyoxime. After standing until cool the mixture is filtered and diluted with 10 times its volume of water; it should be refiltered if a turbidity develops upon standing. No information is given concerning the accuracy of the titration though a good color change is reported with 0.1 N solutions. The titration must be carried out very slowly, with thorough shaking near the end-point, and the titration error is likely to be large, especially with more dilute solutions.

(3) Pierce and Coursey[98] applied the Denigès method to the determination of chloride. The chloride is first precipitated with an excess of silver nitrate and is filtered, washed, and dissolved in ammonia. The solution is diluted to an ammonia concentration of 0.25 N or less and the silver is titrated with cyanide solution, potassium iodide being added as indicator and the end-point being reached when the turbidity has nearly disappeared.

Determination of Metals with Cyanide Solution: The argentometric determination of cyanide has been applied to the estimation of various metals with which cyanide forms complexes, particularly nickel, cobalt, copper, and zinc. Some methods which have been proposed for nickel and cobalt are described below.

Determination of Nickel Alone: Kolthoff and Griffith[99] dissolve the nickel salt (1 to 75 mg. of nickel) in 50 to 70 ml. of water, add 5 ml. of 6 N ammonia, 1 g. of ammonium sulfate, and 1 ml. of 25% potassium iodide solution, and titrate with potassium cyanide solution of strength appropriate to the quantity of nickel expected (0.005 to 0.2 M). When the blue-green color of the nickel ammonia complex fades, a measured small volume (3 or 4 drops) of standard silver nitrate solution is introduced and the titration is continued slowly with shaking until the turbidity of silver iodide disappears. The change is recognized most easily if the turbidity is observed against a black background, with a strong light entering from the side. One millimole of nickel requires four millimoles of cyanide; a correction is applied for the amount of silver nitrate used on the basis that one millimole of silver requires two millimoles of cyanide.

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[97] A. R. Ubbelohde, *Analyst,* **59,** 339 (1934).

[98] J. S. Pierce and J. L. Coursey, *Ind. Eng. Chem., Anal. Ed.,* **4,** 64 (1932).

[99] I. M. Kolthoff and F. S. Griffith, *J. Phys. Chem.,* **42,** 542 (1938). See also T. Moore, *Chem. News.,* **72,** 92 (1895); H. Brearley and H. Jervis, *ibid.,* **78,** 177, 190 (1898); H. Grossmann, *Chem.-Ztg.,* **32,** 1223 (1908).

Notes: (1) Under the recommended conditions the end-point can be recognized to within 0.04 ml. of 0.02 M potassium cyanide solution. With about 75 mg. of nickel the error need not exceed 0.1%, with 30 mg., 0.3%, and with 1.5 mg., 1%. Up to 30 mg. of zinc may be present without causing interference.

(2) To prevent the interference of iron and chromium, as in the analysis of nickel steels, one may add an excess of ammonium citrate.[100] The procedure has been investigated by Boyer,[101] who recommends titrating at a temperature of 30°C. and using a photoelectric titrimeter to reveal the end-point. An excess of cyanide is added and titrated back with standard silver nitrate solution to a faint permanent turbidity. Approximate corrections may be applied for the presence of known small quantities of cobalt or copper; roughly 1 Co ≡ 5 CN while 1 Cu ≡ 3.5 CN.

Determination of Cobalt (and Nickel): Evans[102] recommends cyanide titration as one of the most accurate and simple methods for determining cobalt. In his procedure the sum of the cobalt and nickel is found, then the nickel is determined alone and the cobalt calculated by difference. The cyanide solution, containing 4.8 g. of potassium cyanide and about 3 g. of sodium hydroxide per liter, is standardized (as explained below) against silver nitrate solution. If the latter is made up to contain 5.792 g. of silver nitrate per liter, 1 ml. is equivalent to 1.00 mg. of nickel or to 0.803 mg. of cobalt.

The cobalt is brought into solution in acid, nearly neutralized, made to a volume of about 100 ml., and treated with 20 ml. of saturated borax solution and 10 ml. of 4% potassium iodide. Cyanide is added from a burette until the solution is only slightly turbid; if V ml. has been introduced at this point more cyanide is run in until the total volume used is $(1.3\ V + 5)$ ml.; 10 ml. of 10% sodium carbonate is added and a rapid stream of air is passed through the solution for 6 minutes, as a result of which cobalt is oxidized and combined with cyanide in a ratio of 1:5. The time should be controlled carefully, for the change is not complete before 5 minutes have elapsed and the results are high if more than 7 minutes are allowed. 10 ml. of 1:1 ammonia and 25 ml. of 20% ammonium chloride are added to the mixture and any leakage from the cyanide burette is also washed in (from a small beaker kept under the burette during the oxidation period). Silver nitrate is then added from another burette until a permanent turbidity appears, whereupon just enough cyanide is introduced to clarify the mixture. This is the end-point; both burettes are read and refilled, then a volume of cyanide 0.5 ml. less than that previously taken is run into the titrated solution. This is again titrated with silver nitrate to a turbidity and back to clear with cyanide. Each solution is added dropwise until finally just as much cyanide has been used as in the original titration and the mixture is still at an end-point. The difference between the volumes of silver nitrate used in this standardization and the original titration represents the silver equivalent of the cobalt (and nickel) present.

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[100] See, for example, *A. S. T. M. Methods of Chemical Analysis of Metals*, American Society for Testing Materials, Philadelphia 1939, p. 34.

[101] W. J. Boyer, *Ind. Eng. Chem., Anal. Ed.*, **10**, 175 (1938).

[102] B. S. Evans, *Analyst*, **62**, 363 (1937).

In order to determine nickel in the presence of cobalt, Evans adds 2–3 ml. of saturated potassium cyanide solution and a few drops of 20% hydrogen peroxide to an ammoniacal solution of the metals. Boiling for 5 minutes converts cobalt into unreactive cobalticyanide and leaves nickel as a nickelous cyanide complex. 20 ml. of 20% ammonium chloride is added and the solution is boiled for 15 minutes. While it is still warm, 10 ml. of 1:1 ammonia and 10 ml. of hydrogen peroxide are introduced and boiling is continued for 10 minutes longer. The excess peroxide should be decomposed, but the loss of too much ammonia should be avoided lest some difficultly soluble nickel cobalticyanide form. After cooling the solution, one adds several drops of 35% citric acid, 10 ml. each of 1:1 ammonia and 4% potassium iodide, and enough water to bring the volume to 250–300 ml. The solution is titrated with potassium cyanide until the blue color is practically dispelled, then 1 or 2 ml. of standard silver nitrate is run in from a burette. The turbidity which appears is clarified with cyanide, an excess of the latter being necessary if nickel cobalticyanide is present. Finally the silver nitrate and cyanide are adjusted so that the mixture just remains clear. The quantity of silver equivalent to the nickel present is found after standardization of the cyanide solution as described in the preceding paragraph.

Evans also describes a method of determining cobalt in steel, in which the separation of cobalt from iron is carried out with α-nitroso-β-naphthol. Details are to be found in the original article.

5. Argentometric Determination of Other Substances.—In addition to the halide and pseudohalide ions, many other anions such as carbonate, iodate, chromate, phosphate, arsenate, oxalate, succinate, and higher fatty acids may be precipitated with an excess of silver nitrate under the proper conditions, and the excess of silver determined by the Volhard method after filtration. If the solubility product of the silver salt is known (*cf.* Vol. I, p. 287) one may calculate the concentration of silver nitrate needed to repress the solubility sufficiently. The calculated value, however, should be verified experimentally. Practical details concerning determinations of some of these anions are given in this section.

Phosphate: The solubility product of tertiary silver phosphate, Ag_3PO_4, is approximately 10^{-21}. The exact value is difficult to determine.[103] Phosphate solutions which are neutral to phenolphthalein contain very few tertiary phosphate ions, the secondary ions predominating. Upon addition of silver nitrate, hydrogen ions are liberated:

$$HPO_4^{=} + 3Ag^+ \rightleftarrows Ag_3PO_4 + H^+$$

These decrease the concentration of tertiary phosphate ions and increase the solubility of silver phosphate. In order to determine phosphate argentometrically, one should keep the hydrogen-ion concentration small so that the precipitation may be complete.

Mohr[104] treated the phosphate solution with an excess of silver nitrate, then neutralized carefully with sodium hydroxide and titrated the excess silver. Perrot[105] improved the method by precipitating the phosphate in the presence of ammonium acetate. Holleman[106] recommended sodium acetate as a buffering agent. The procedures have been studied by various workers[107]; according to Berthelot[108] the solution must be neutral to phenolphthalein after precipitation. This neutralization must be performed carefully lest silver hydroxide be formed. In a 0.01 M silver solution the solubility product of silver hydroxide ($S_{AgOH} = 4 \times 10^{-8}$) is exceeded at a p_H of 9. Kolthoff[103] made the following recommendations concerning phosphate determinations:

(*a*) The neutral or slightly acid phosphate solution is treated with an excess of standard silver nitrate solution and neutralized with chloride-free alkali to the transition color of phenol red, then the suspension is diluted to a definite volume and is filtered. The first portion of the filtrate is rejected and an aliquot part of the remainder is titrated by the Volhard method.

(*b*) A phosphate solution made just alkaline to methyl orange may be treated with excess silver nitrate followed by at least 2 g. of sodium acetate. The mixture is then diluted, filtered, and titrated as in (*a*).

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[103] I. M. Kolthoff, *Pharm. Weekblad*, **59**, 205 (1922).

[104] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethoden*. 1st ed., Part 2, Vieweg, Braunschweig 1860, p. 89.

[105] E. Perrot, *Compt. rend.*, **93**, 495 (1881).

[106] A. F. Holleman, *Rec. trav. chim.*, **12**, 1 (1893).

[107] F. Kratschmer and Sztankovánszky, *Z. anal. Chem.*, **21**, 523 (1882). W. Strecker and P. Schiffer, *ibid.*, **50**, 495 (1911). J. M. Wilkie, *J. Soc. Chem. Ind.*, **28**, 68, 464 (1909); **29**, 794 (1910).

[108] M. Berthelot, *Ann. chim. phys.*, **25**, 164 (1902).

Note: Salts of calcium, magnesium, and ammonium do not interfere. The determination is accurate to within about 0.5%. Alternatively the silver phosphate precipitate may be washed, dissolved in nitric acid, and titrated by the Volhard method, but an error of 1% or more may be caused by losses of silver phosphate during the washing. The solubility of silver phosphate, expressed in terms of silver, is given for various p_H values in the accompanying table.

SOLUBILITY OF SILVER PHOSPHATE IN WATER AND VARIOUS BUFFERED SOLUTIONS[109]

$[Ag^+]$	p_H	Buffer
4.4×10^{-3}	5.2	None
3.0×10^{-3}	5.7	Acetate
2.2×10^{-3}	6.0	Acetate
1.8×10^{-3}	7.0	Acetate
1.6×10^{-3}	7.6	Acetate
1.2×10^{-3}	7.8	Sodium bicarbonate
3.5×10^{-5}	10.8	Magnesium oxide suspension
1.0×10^{-5}	11.2	0.1 N sodium carbonate

Rosin[110] recommended that the free acid formed during precipitation of silver phosphate should be neutralized with a slight excess of zinc oxide. Maurina[111] obtained irregular results with the oxide and recommended the use of zinc hydroxide instead. The latter is prepared by shaking finely powdered zinc carbonate for 20 to 30 minutes with twice the theoretical quantity of 10% potassium hydroxide solution and then washing with water. Stearn, Farr, and Knowlton[112] also found the use of zinc oxide unsatisfactory; they obtained good results by adding the theoretical quantity of sodium hydroxide to the phosphate solution before precipitation. For example, they titrate phosphoric acid to the disodium salt, using phenolphthalein and titrating the cold solution in the presence of sodium nitrate, then they add half again as much sodium hydroxide in order to form the trisodium salt before introducing silver nitrate.

Arsenate: Arsenic acid, like phosphoric acid, forms a slightly soluble silver salt and may be determined by the Volhard method under similar conditions.

McCay[113] developed a procedure for determining arsenic in the presence of antimony. Both elements are brought to the pentavalent state and an excess of hydrofluoric acid is added to bind the antimony. The solution is made slightly alkaline with ammonia and the arsenate is precipitated with an excess of standard silver nitrate. After filtration, nitric acid is added and the excess silver titrated by the Volhard method.

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[109] I. M. Kolthoff, *Pharm. Weekblad,* **59,** 205 (1922).

[110] J. Rosin, *J. Am. Chem. Soc.,* **33,** 1099 (1911).

[111] F. A. Maurina, *J. Am. Pharm. Assoc.,* **17,** 668 (1928).

[112] A. E. Stearn, H. V. Farr, and N. P. Knowlton, *Ind. Eng. Chem.,* **13,** 220 (1921).

[113] L. W. McCay, *J. Am. Chem. Soc.,* **50,** 368 (1928).

Pomerantz and McNabb[114] precipitate silver arsenate under the conditions recommended by Hillebrand and Lundell.[115] From 0.04 to 0.23 g. of potassium dihydrogen arsenate is dissolved in 100 ml. of water in a 400 ml. beaker; the solution is made slightly acid with nitric acid and enough 0.1 N silver nitrate is added to provide an excess of 10 ml. 10% sodium hydroxide is added until the solution becomes turbid, then dilute nitric acid is introduced dropwise until it is clear again. The mixture is buffered with 10 ml. of saturated sodium acetate solution, heated to boiling, cooled, and filtered. The precipitate is washed with saturated silver arsenate solution until the washings give only a faint opalescence with hydrochloric acid. Pomerantz and McNabb dissolve the precipitate in 30 ml. of warm 2 N nitric acid followed by hot water, add enough 6 N sulfuric acid to make the solution 1–2 N, dilute to 120–150 ml. with water and titrate the silver with standard 0.1 N iodide. 3 ml. of 0.5% starch solution and 3 drops of 0.1 N ceric solution are added to furnish the indicator action.[116]

Sulfide: Silver sulfide is very slightly soluble, even in an excess of ammonia. Application of this slight solubility is made in the determination of lead, bismuth, copper, zinc, and cadmium as sulfides:

$$ZnS + 2Ag^+ \rightarrow Ag_2S + Zn^{++}$$

The metal sulfide is shaken with an excess of silver nitrate and filtered, after which silver is back-titrated in an aliquot portion of the filtrate.

Allyl Isothiocyanate: The argentometric sulfide titration may also be applied to the assay of mustard oil. The sulfur of allyl isothiocyanate is quantitatively precipitated as silver sulfide upon heating with silver nitrate in ammoniacal solution:

$$C_3H_5NCS + NH_3 \rightarrow \underset{(\textit{Thiosinamine})}{C_3H_5NHCSNH_2}$$

$$C_3H_5NHCSNH_2 + 2Ag^+ + 2NH_3 \rightarrow \underset{\textit{Allyl cyanamide}}{C_3H_5NHCN} + Ag_2S + 2NH_4^+$$

Details of the procedure are given in reference works on pharmaceutical chemistry.[117]

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[114] A. Pomerantz and W. M. McNabb, *Ind. Eng. Chem., Anal. Ed.*, **8**, 466 (1936).

[115] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis.* Wiley, New York 1929, p. 216.

[116] A. Bloom and W. M. McNabb, *Ind. Eng. Chem., Anal. Ed.*, **8**, 167 (1936).

[117] *United States Pharmacopoeia,* 12th Rev., Mack Printing Co., Easton, Pa. 1942, p. 46.

Selenite: Ripan-Tilici[118] titrates selenite with silver nitrate, using fluorescein as adsorption indicator. The solution, about 50 ml. in volume and 0.01 N with respect to selenite, is first neutralized to a p_H of 9.5 to 9.6 (thymolphthalein). The titration is carried out with 0.05 or 0.1 N silver nitrate and near the end-point the mixture should be shaken well; the color change is to red. Diphenylcarbazone, with a color change from red to blue, may also be used at the same p_H.

A procedure for the determination of elemental selenium is based upon its oxidation and reduction in warm ammoniacal silver nitrate solution:[119]

$$6Ag^+ + 3Se + 6NH_3 + 3H_2O \rightarrow 2Ag_2Se + Ag_2SeO_3 + 6NH_4^+$$

After the reaction has been brought about by boiling for a few minutes, the mixture is treated with excess nitric acid. Silver selenite dissolves and the liberated silver, along with the initial excess, is titrated back by the Volhard method. In the complete process, therefore, four atoms of silver are equivalent to three of selenium:

$$4Ag^+ + 3Se + 3H_2O \rightarrow 2Ag_2Se + H_2SeO_3 + 4H^+$$

Arsine: In this case, as well as in several others, the oxidizing action of silver nitrate is used as the basis for an argentometric determination. Křepelka and Fanta[120] determine arsine by passing it through a warm solution of ammoniacal silver nitrate:

$$AsH_3 + 8AgNO_3 + 11NH_3 + 4H_2O -$$
$$(NH_4)_3AsO_4 + 8Ag + 8NH_4NO_3$$

Their procedure may be applied to the estimation of small quantities of arsenic after reduction to arsine by the action of zinc metal and a little stannous chloride and ferrous sulfate in sulfuric acid solution (Gutzeit reaction).

Procedure: The arsine, equivalent to not more than 0.3 mg. of arsenic, is absorbed in 10 ml. of 0.1 N silver nitrate containing 5 ml. of 15% ammonia. Oxidation to arsenate takes place slowly and the suspension must be kept on a steam bath for 4 hours, 2 ml. of 15% ammonia being added each hour. It is allowed to cool for 2 hours, then is treated with 2 ml. more of 15%

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[118] R. Ripan-Tilici, *Z. anal. Chem.*, **117**, 326 (1939). Silver selenate is also slightly soluble; *cf.* R. Ripan, *ibid.*, **124**, 38 (1942).

[119] K. Friedrich, *Z. angew. Chem.*, **15**, 852 (1902). H. Frerichs, *Arch. Pharm.*, **240**, 656 (1902).

[120] J. H. Křepelka and J. Fanta, *Collection Czechoslov. Chem. Commun.*, **9**, 47 (1937).

ammonia and filtered. The silver precipitate is dissolved in nitric acid and determined by a Volhard titration with 0.01 N thiocyanate (Křepelka and Fanta used a nephelometric method).

Note: In this way as little as 0.02 mg. of arsenic may be determined within 10%. The accuracy is better with larger amounts but because of the slow absorption of arsine in ammoniacal solution the procedure is not suitable for quantities greater than about 0.3 mg.

The reaction of arsine with silver nitrate in neutral or slightly acid solution was employed by Mai and Hurt,[121] who gave the following equation:

$$AsH_3 + 6AgNO_3 + 3H_2O \rightarrow H_3AsO_3 + 6Ag + 6HNO_3$$

According to Reckleben, Lockemann, and Eckhardt,[122] the reaction is not quantitative. Křepelka and Fanta verified this and found that good results are possible only through compensating errors. Part of the silver is reduced by hydrogen (high values) while some of the arsenic may be precipitated as Ag_3As (low values). The general tendency is toward low results.

Phosphine: A procedure similar to the arsine absorption method of Mai and Hurt[121] has been used by Schut and Jansen[123] for the determination of phosphine liberated from ferrosilicon samples by acid. They note that when the gas is absorbed in 25 ml. of 0.1 N silver nitrate the precipitate contains phosphorus as well as silver, but that substantially six moles of silver nitrate are required for one of phosphine. They determine excess silver in the filtrate by neutralizing with magnesium oxide, adding an excess of standard sodium chloride and titrating the latter by Mohr's method.

Xanthate: An alkyl xanthate (which is readily formed from carbon disulfide and an alcoholic solution of a strong alkali) reacts with silver nitrate to give a slightly soluble silver salt:[124]

$$C_2H_5OCS_2^- + Ag^+ \rightarrow C_2H_5OCS_2Ag$$

Makens[125] recommends the following method for determining xanthates argentometrically.

Procedure: To about 0.5 g. of the xanthate in 100 ml. of water one adds a slight excess of 0.1 N silver nitrate, from a burette. 30 ml. of 10% ferric nitrate is introduced and the excess of silver is titrated at once with standard thiocyanate solution. Better, an excess of thiocyanate is added quickly and back-titrated with silver nitrate.

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[121] C. Mai and H. Hurt, *Z. Untersuch. Nahr. u. Genussm.*, **9**, 193 (1905); *Z. anal. Chem.*, **44**, 321 (1905).

[122] H. Reckleben, G. Lockemann, and A. Eckhardt, *Z. anal. Chem.*, **46**, 671 (1907).

[123] W. Schut and J. D. Jansen, *Rec. trav. chim.*, **51**, 321 (1932).

[124] A. Reychler, *Bull. soc. chim. Belg.*, **37**, 165 (1928).

[125] R. F. Makens, *J. Am. Chem. Soc.*, **57**, 405 (1935).

Note: If the xanthate is allowed to stand in the presence of silver nitrate, it decomposes:

$$C_2H_5OCS_2Ag + 2Ag^+ + H_2O \rightarrow C_2H_5OCOSAg + Ag_2S + 2H^+$$
$$2C_2H_5OCOSAg + H_2O \rightarrow 2C_2H_5OH + Ag_2S + COS + CO_2$$

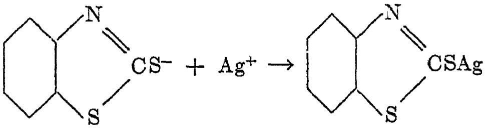
Mercaptans: Borgstrom and Reid[126] utilized the formation of silver mercaptide for the determination of mercaptans in naphthas. Malisoff and Anding[127] modified their method in order to secure better reproducibility.

Procedure: Treat the sample in a glass-stoppered Erlenmeyer flask with 5 to 10 ml. of methanol and an excess of 0.005 to 0.05 N silver nitrate, depending upon the quantity of mercaptan expected. Shake well and add 2 ml. of ferric alum indicator solution (40 g. of ferric alum and 20 ml. of 6 N nitric acid per 100 ml., boiled to remove nitrogen oxides and then diluted with 300 ml. of water). Titrate with standard thiocyanate solution to a faint pink, then add a small excess of silver nitrate and titrate again with thiocyanate to a very faint pink. The mixture should be shaken constantly during the titrations.

Note: Hydrogen sulfide, if present, may be removed by preliminary treatment with cadmium chloride in slightly acid solution. Elemental sulfur does not interfere, according to Schindler, Ayers, and Henderson,[128] and had better be left in the hydrocarbon solution than removed by shaking with mercury as is sometimes recommended. Mercuric sulfide adsorbs mercaptans.

Malisoff and Anding[129] called attention to the fact that mercaptans are readily oxidized to disulfides when exposed to diffused daylight. Samples should be kept in the dark and analyzed as promptly as possible. The procedure gives results which are generally reproducible to within 2%.

Mercaptobenzothiazole: This compound is important commercially as a vulcanizing agent. Its silver salt is only slightly soluble in weakly acid or ammoniacal solution, but more so in strong acid. Uschakow and Galanow[130] studied both the Volhard titration and a direct titration using dichlorofluorescein as indicator in the presence of ammonia. In either case the reaction is:



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[126] P. Borgstrom and E. E. Reid, *Ind. Eng. Chem., Anal. Ed.*, **1**, 186 (1929).

[127] W. M. Malisoff and C. E. Anding, Jr., *Ind. Eng. Chem., Anal. Ed.*, **7**, 86 (1935).

[128] H. Schindler, G. W. Ayers, and L. M. Henderson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 326 (1941).

[129] W. M. Malisoff and C. E. Anding, Jr., *loc. cit.* See also M. W. Tamele, L. B. Ryland, and V. C. Irvine, *Ind. Eng. Chem., Anal. Ed.*, **13**, 618 (1941).

[130] M. I. Uschakow and A. S. Galanow, *Z. anal. Chem.*, **99**, 185 (1934).

Procedure for Volhard Titration: A sample containing about 0.25 g. of mercaptobenzothiazole is made barely acid with dilute nitric acid and is treated with an excess of standard silver nitrate. Ferric alum indicator is added, along with 30 to 40 ml. of ether (to make the color change more distinct), and the excess of silver is titrated back with thiocyanate. It would seem preferable here to filter off the silver salt before back-titrating the solution. The filtrate may then be acidified more strongly before titration.

Procedure with Dichlorofluorescein: The sample, containing about 0.15 g. of mercaptobenzothiazole, is dissolved in 7.5 to 10 ml. of a 2% solution of ammonia in ethanol. While stirring constantly, one adds 150 ml. of water and 3 drops of 0.5% dichlorofluorescein solution. The mixture is titrated with 0.05 N silver nitrate, the color shifting gradually from green to yellow-green at first. Near the equivalence-point a light pink precipitate appears which suddenly becomes a bright pink. The end-point is reached when this sudden transition occurs and the color does not change further upon addition of a little more silver nitrate. Since the results are normally about 0.9% low, a correction of this magnitude should be applied.

Theobromine: According to Mikó[131] the theobromine content of a theobromine–sodium salicylate preparation may be determined argentometrically.

Procedure: An 0.5 g. sample is allowed to stand for a few minutes in 10 ml. of water plus 1 ml. of 5 N nitric acid, then 2 ml. of 5 N ammonia and 30 ml. of 0.1 N silver nitrate are added. The mixture is shaken well, boiled for 15 minutes, cooled, and diluted to 100 ml. in a volumetric flask. After being thoroughly mixed it is filtered and the first 25 ml. is discarded. An aliquot portion of 50 ml. is acidified with 10 ml. of 5 N nitric acid and titrated by the Volhard method. Each milliliter of 0.1 N silver consumed represents 18.01 mg. of theobromine.

Barbituric Acid Derivatives: Alkylated barbiturates (in which the substituents are not on the nitrogen) form insoluble silver salts. Veronal, for example, forms a disilver salt with silver nitrate in weakly alkaline solution:

$$C_8H_{12}N_2O_3 + 2Ag^+ \rightarrow C_8H_{10}Ag_2N_2O_3 + 2H^+$$

The acid liberated must be neutralized, for which purpose borax is a suitable buffer according to Schulek and Rózsa.[132]

Procedure: From 0.1 to 0.15 g. of diethyl- or diallylbarbituric acid is dissolved by boiling with 25 ml. of 5% borax solution in a 125 ml. Erlenmeyer flask. 1 ml. of 10% potassium chromate solution is added and the hot solution is titrated with 0.1 N silver nitrate until the yellow-green suspension assumes a red color which is stable upon boiling. 1 ml. of 0.1 N silver nitrate is equivalent to 9.20 mg. of diethylbarbituric acid or to 10.40 mg. of the diallyl compound. Schulek and Rózsa give methods for separating the barbiturates from theobromine, theophylline, and organic acids.

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[131] J. v. Mikó, *Pharm. Monatsh.*, **14,** 279 (1933).

[132] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **112,** 404 (1938).

Iodoform: In alcoholic solution iodoform reacts slowly with silver nitrate, quantitatively forming silver iodide:

$$CHI_3 + 3Ag^+ + H_2O \rightarrow 3AgI + 3H^+ + CO \text{ (or } HCOOH)$$

On this reaction Kunke[133] has based a procedure which is reported to yield excellent results.

Procedure: Approximately 0.25 g. of iodoform is dissolved in 40 ml. of 95% ethanol in an Erlenmeyer flask. 40 ml. of 0.1 N silver nitrate and 10 ml. of concentrated nitric acid are added and the mixture is shaken repeatedly during a 5 minute period. It is then allowed to stand for 2 hours with occasional shaking to coagulate the silver iodide. The excess silver is titrated with thiocyanate, each milliliter of 0.1 N silver consumed corresponding to 13.13 mg. of iodoform.

Aldehydes: That the carbonyl group of an aldehyde may be oxidized to a carboxyl group by ammoniacal silver nitrate solution, with formation of an equivalent quantity of silver, is well known. Several procedures for the determination of aldehydes have been based upon this fact.[134] According to Ponndorf[135] there are disadvantages in using an ammoniacal solution. The active reagent is not the silver–ammonia complex but the small amount of silver oxide formed by hydrolysis; ammonia hinders the reaction. Ponndorf therefore developed several methods in which finely divided silver oxide is used without ammonia.

Procedure for Acetaldehyde Determination: In a 100 ml. volumetric flask are placed 0.5 ml. of 1 N magnesium sulfate, 25 ml. of 0.1 N silver nitrate, and 10 ml. of the solution to be analyzed, containing from 5 to 45 mg. of acetaldehyde. Into this, with continuous shaking, is run 13 ml. of 0.2 N sodium hydroxide (carbonate-free) from a burette of rapid outflow. The flask is stoppered and shaken vigorously for 5 minutes, then 5.7 to 6.0 ml. more of 0.2 N sodium hydroxide is introduced and the mixture is shaken again for 5 minutes. The stopper is removed and washed with 1 ml. of water. 5 ml. of 1 N potassium hydroxide is added at the rate of 1 ml. in 10 seconds, the flask being shaken meanwhile and for 2 minutes afterwards. The suspension is neutralized by the gradual addition of 5 ml. of 20% sulfuric acid, cooled to room temperature, diluted to the mark, mixed well, and filtered. The silver present in 50 ml. of the filtrate is titrated with standard potassium iodide solution, using starch–iodine indicator (p. 274). The initial titer of the silver solution is ascertained in a blank determination.

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[133] W. F. Kunke, *J. Assoc. Official Agr. Chem.*, **14**, 370 (1931).

[134] B. Tollens, *Ber.*, **15**, 1828 (1882); **16**, 917, 921 (1883). R. Orchard, *Analyst*, **22**, 4 (1897). L. Vanino, *Z. anal. Chem.*, **40**, 720 (1901). W. Steppe and R. Fricke, *Z. physiol. Chem.*, **116**, 293 (1921). R. Fricke, *ibid.*, **118**, 241 (1922).

[135] W. Ponndorf, *Ber.*, **B64**, 1913 (1931).

Notes: (1) The presence of the total quantity of alkali specified is necessary to cause the reaction to proceed rapidly enough. The alkali is not added all at once, however, since it would then favor condensation reactions of the aldehyde. Addition of magnesium sulfate also serves to increase the reaction velocity, since in its presence the silver oxide is coprecipitated with magnesium hydroxide and a large surface is exposed.

(2) Under good conditions the determination is accurate to about 0.2% with 36 mg. of acetaldehyde or to 1% with 5 mg. With smaller quantities the above procedure is not reliable. Ponndorf[135] developed micro methods suitable for 0.001 to 0.08 mg. or for 0.1 to 0.4 mg. In these cases he employed colloidal silver oxide suspensions stabilized with silicic acid or alum. His paper should be consulted for details.

(3) The procedure may also be applied to other aldehydes such as formaldehyde or hexoses which react as rapidly as acetaldehyde. With glucose it was found that one ml. of 0.1 N silver nitrate is equivalent to 1.41 mg. of sugar; that is, each mole of glucose reduces 12.75 moles of silver nitrate. Aldehydes which react more slowly may be determined by the procedure below.

Procedure for Propionaldehyde or Benzaldehyde: To 50 ml. of aldehyde solution in a 250 ml. volumetric flask are added 45–50 ml. of 0.1 N silver nitrate, 12 ml. of 0.1 N barium hydroxide, and 67 ml. of 0.1 N sodium hydroxide, with shaking. The mixture is shaken for 2 minutes and then heated for 5 minutes on a steam bath. Alkali is added in the following steps, after each of which the suspension is heated, meanwhile being shaken well, for 5 minutes on the steam bath. The first addition consists of 10 ml. of 1 N potassium hydroxide and the second of 10 ml. of 50% potassium hydroxide. After the contents of the flask have been allowed to cool, 15 ml. of 50% sulfuric acid is introduced gradually, with cooling, and the solution is diluted to the mark, mixed, and filtered. A 200 ml. portion is titrated with 0.1 N potassium iodide. The error is said to be from 0.5 to 1%.

Carbon Monoxide: According to Manchot and Scherer[136] a mixture of silver nitrate, alkali and pyridine reacts rapidly with carbon monoxide:

$$CO + Ag_2O \rightarrow CO_2 + 2Ag$$

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[136] W. Manchot and O. Scherer, *Ber.*, **B60**, 326 (1927). W. Manchot and G. Lehmann, *ibid.*, **B64**, 1261 (1931).

Procedure: 50 milliliters each of 0.1 N silver nitrate and 0.15 N sodium hydroxide are mixed in a thick-walled, glass-stoppered bottle and enough diluted pyridine solution to dissolve the silver oxide is added immediately. The bottle is then evacuated and the sample to be analyzed is allowed to flow in from a gas burette. After an initial vigorous shaking, the bottle is kept at about 65°C. for 30 minutes, with further shaking at intervals. The mixture is barely acidified with acetic acid and filtered, then the filtrate is treated with nitric acid and the excess silver is titrated by the Volhard method. Alternatively the precipitated silver may be washed, dissolved in nitric acid, and titrated. Each milliliter of 0.1 N silver nitrate corresponds to 1.4 mg. of carbon monoxide.

6. Methods for the Titration of Silver.—The principles of these procedures, together with considerations regarding the reagents and standard solutions, have been given earlier in this chapter. Further details of interest primarily in the determination of silver are presented here.

(*a*) ***Volhard Method:*** The silver solution which is to be titrated should contain at least 10 ml. of 4 N nitric acid and 1–2 ml. of saturated ferric ammonium sulfate solution per 100 ml. Standard thiocyanate solution is added from a burette until a temporary reddish brown color appears, then the mixture is shaken vigorously and titrated further until the color no longer disappears. The necessary excess of 0.1 N thiocyanate amounts to 0.01 or 0.02 ml. per 100 ml. of solution.

Notes: (1) The nitric acid added should be free from nitrogen oxides which react with thiocyanate. In assaying metallic silver, the oxides formed during solution of the metal may be expelled by boiling. A small trace remaining causes no serious interference.

(2) Salts of mercury interfere by forming a slightly dissociated thiocyanate (see p. 336); they may be removed by ignition. Recognition of the end-point is difficult in the presence of much copper, nickel, or cobalt.[137] None of the other metals, except palladium, interferes with the accuracy of the determination.

(3) The Volhard method has not been widely applied in mint laboratories, because the procedure of Gay-Lussac (*c*) is more exact. Rose[138] urged the use of the Volhard method and recommended filtering off the silver thiocyanate when nearly all of the silver has been precipitated. The end-point may then be seen more clearly. Appreciable adsorption of silver ions by the precipitate, however, may lead to an error which should not be disregarded.[139]

(*b*) ***Fajans Method:*** Fajans and Wolff[140] showed that silver may be titrated with potassium bromide quite accurately in acid solution, using Rhodamine 6G (the hydrochloride of a basic dye) as indicator. As long as silver ions are present in excess, the indicator cation is not noticeably adsorbed by silver bromide. At the equivalence-point, or especially after a very slight excess of bromide has been added, the precipitate adsorbs the dye strongly and thereby acquires a blue-violet color. The end-point can be perceived quite sharply in a dilute nitric acid solution, though the acidity should not exceed 0.5 N. Partial coagulation of the silver bromide takes place shortly before the end-point, but the solid remains uncolored.

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[137] *Cf.* F. P. Dewey, *Ind. Eng. Chem.*, **6**, 728 (1914).

[138] T. K. Rose, *J. Chem. Soc.*, **77**, 232 (1900).

[139] C. Hoitsema, *Z. angew. Chem.*, **17**, 647 (1904).

[140] K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, **137**, 241 (1924).

According to Fajans and Wolff the mean accuracy is approximately 0.1%, with individual variations of ±0.3%. Kolthoff's experience indicates that the change is distinct even with 0.01 N solutions.

In place of Rhodamine 6G, phenosafranine may be employed.[141] While excess silver is present the silver bromide is colored blue; at the equivalence-point it becomes red. The solution must contain nitrate ions in order for the color change to take place. 1 ml. of 0.005% phenosafranine is used for 50 ml. of 0.05 N silver solution. Nitric acid decreases the accuracy of the titration, yet the error need not exceed 0.4% in 0.04 N acid. Large amounts of zinc cause the result to be about 0.8% low; lead, on the contrary, scarcely interferes at all.

Hodakow[142] titrates silver with chloride, using methyl violet or crystal violet as indicator. The color change is from blue to pink, the dye being adsorbed at or just after the equivalence-point. The change is not completely reversible.

Berry and Durrant[143] make use of tartrazine in the titration of silver with bromide. The precipitate first adsorbs the dye and remains yellow until the end-point, when the tartrazine is displaced and produces a greenish yellow color in the liquid. The first perceptible green color appears 0.2 to 0.25% before the equivalence-point; by titrating to a deeper green the result may be brought to within 0.1% of the theoretical. The change is quite distinct but apparently is not entirely reversible. Berry later found[144] that pyrazolone yellow (probably pyrazolone yellow J, British Colour Index No. 636) behaves in the same way as tartrazine.

For titrating silver with thiocyanate in weakly alkaline solution, Uzumasa and Miyake[145] employ sodium alizarin sulfonate (yellow to pink), phenolphthalein (pink to purple), cochineal (purple to green), or phenol red (red to violet) as indicator.

(*c*) ***Gay-Lussac—Mulder Method:*** The theoretical basis for this method of titrating silver nitrate with sodium chloride has been discussed on page 240. The method is one of the most accurate and precise of all volumetric determinations and is used in various mint laboratories. Generally the titration is carried out by precipitating most of the silver with a strong standard solution of chloride, then adding diluted chloride solution until a point is reached at which no further turbidity appears. According to

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[141] H. McColloch Weir, *Dissertation,* Munich 1926.

[142] I. W. Hodakow, *Z. physik. Chem.,* **127,** 43 (1927); **129,** 128 (1927).

[143] A. J. Berry and P. J. Durrant, *Analyst,* **55,** 613 (1930).

[144] A. J. Berry, *Analyst,* **57,** 511 (1932).

[145] Y. Uzumasa and Y. Miyake, *J. Chem. Soc. Japan,* **54,** 624 (1933); *Chem. Abstracts,* **27,** 5673 (1933).

Hoitsema[146] the end-point occurs slightly beyond the equivalence-point; he found that no turbidity appears after the silver concentration has dropped to 1.6×10^{-6} M. From this the excess of chloride present may be calculated:

The solubility product of silver chloride is 1.7×10^{-10} at 25°C. If the excess chloride added corresponds to a concentration of a moles per liter, and if the silver concentration is 1.6×10^{-6} molar (actually it is slightly lower, for some of the silver chloride is undissolved at the limit of visibility), the following equation applies:

$$(a + 1.6 \times 10^{-6})\ (1.6 \times 10^{-6}) = 1.7 \times 10^{-10}$$
$$a = 1.0 \times 10^{-4}$$

This excess, a, would be equivalent to 1.0 ml. of 0.01 N chloride per 100 ml. of solution. Experimentally, Hoitsema found the absence of turbidity after an excess of 0.5 ml. had been added. In the titration of 0.1 N silver nitrate with 0.1 N sodium chloride, the error amounts to 0.1%. The titration error is customarily avoided in mint laboratories by standardizing the sodium chloride solution against pure silver under identical conditions.

In order to titrate exactly to the equivalence-point, one may, according to Mulder,[146] add sodium chloride solution until a portion of the supernatant liquid gives the same turbidity with a given quantity of chloride as an equal portion does with an equivalent quantity of silver. This method has been used in the Netherlands mint laboratory and was employed by Richards and Wells[147] for atomic weight determinations. While the presence of accompanying electrolytes hastens the separation of silver chloride from its saturated solution, Richards and Wells noted that irregularities might be encountered because of variations in the time required for development of opalescence under different circumstances.

In mint laboratories it is customary to work with an empirical solution of sodium chloride, such that 100 ml. will precipitate 1 g. of silver. This is called a "normal" solution and a portion of it is diluted tenfold to prepare the "decimal" solution finally used in the titration. The silver sample is weighed out to contain very slightly more than 1 g. of pure silver, that is, to correspond closely to 100 ml. of "normal" solution and yet contain a small excess of silver. A reference sample of pure silver is also carried along as a standard, with each determination.

Procedure: The metal sample is placed in a 250 ml. clear glass bottle (provided with a glass stopper) and is dissolved in 10 ml. of concentrated, chloride-free nitric acid, with precautions against loss by spattering. The

[146] C. Hoitsema, *Z. physik. Chem.*, **20**, 272 (1896). See also G. J. Mulder, *Scheikundige Verhandelingen en Onderzoekingen*, Utrecht; German translation (by Grimm), Weber, Leipzig 1859, Vol. I, p. 1, Vol. II, p. 105.

[147] T. W. Richards and R. C. Wells, *J. Am. Chem. Soc.*, **27**, 459 (1905).

mixture may be warmed gently to hasten the solution process, after which the oxides of nitrogen are blown out with air. When the solution is cool, the bottle is wrapped in black paper to prevent the action of light upon silver chloride, then 100 ml. of "normal" chloride solution is allowed to flow in from a vertical Stas pipette (p. 8). In order to coagulate the silver chloride, the bottle is stoppered and shaken for several minutes in a mechanical agitator. The titration is then completed by one of the following methods:

(*a*) The silver chloride adhering to the stopper and sides of the bottle is washed down, the bottle is swirled gently, and the suspension is allowed to settle for a minute or two. From a pipette one adds 0.5 or 1.0 ml. of the "decimal" solution, in such a way that it flows down the wall of the bottle. If the silver has not already been completely precipitated, there appears an opalescence which upon careful stirring spreads throughout the liquid. Recognition of the turbidity is easier if the bottle is held against a black background and illuminated from the side, so that the observation is made by reflected rather than transmitted light. If a turbidity appears it is coagulated by shaking, after which another portion of decimal solution is added. This process is repeated until a fresh portion no longer produces a visible opalescence; the last quantity, which causes no turbidity, is not included in the titration volume.

The precision naturally depends to a great extent upon the quantity of decimal solution which is added at each observation. If a 0.5 ml. portion is used each time, the precision is approximately 0.05%.

(*b*) One may titrate exactly to the equivalence-point, as has been the custom at the Netherlands mint laboratory. Clear supernatant liquid (from a mixture prepared as above) is divided equally between two large test tubes. To one is added 0.25 ml. of decimal chloride solution, and to the other, an equal volume of a "decimal" silver nitrate solution containing 1 g. of silver per liter. At the equivalence-point the two tubes should show identical turbidities. A difference between the turbidities indicates an excess of either chloride or silver; the solutions are then mixed and titrated further with the appropriate decimal solution before being retested in the same way. According to van Heteren[148] the end-point may be recognized to within 0.05 ml. of decimal solution, equivalent to a precision of 0.005%. This is, therefore, one of the most exact volumetric methods available.

(*c*) The intensity or depth of turbidity that is produced by addition of decimal chloride or silver solution to the supernatant liquid may be measured quantitatively in a nephelometer, through comparison with known mixtures. The latter consist of saturated silver chloride solutions having the same electrolyte concentration as the titrated solution, with known quantities of chloride or silver added.

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[148] W. J. van Heteren, private communication.

Notes: (1) Mulder studied the influence of various metals in the Gay-Lussac titration. Mercury is the most objectionable but may be removed easily by ignition. Antimony yields a suspension of colloidal antimonic acid which obscures the end-point; it may be kept in solution by addition of tartaric acid. The same treatment serves to prevent interference by bismuth. According to Levol,[149] alloys containing tin should be dissolved in hot, strong sulfuric acid, since insoluble metastannic acid forms when nitric acid is used.

(2) Gold does not dissolve in nitric or sulfuric acid and if an appreciable quantity is present it may prevent complete solution of the silver. Measures which may be taken to aid in the extraction of silver consist in rolling the alloy to a very thin sheet and boiling with stronger acid, or better, fusing the weighed sample with silver-free cadmium or a known quantity of pure silver, for which correction is later made. In the latter case, the sample weight should be so adjusted that the total silver content after fusion is only 1 g.

(3) Stas[150] proposed that the titration be made with a bromide solution rather than with sodium chloride, since silver bromide is less soluble than silver chloride. A saturated solution of silver bromide does not give a perceptible turbidity when treated with either bromide or silver ions; upon titrating to the point at which no turbidity appears one obtains practically the theoretical result. *In principle, therefore, a bromide solution is to be preferred to a chloride solution, for the determination of silver.* Beckurts[151] states that this modification of the Gay-Lussac method for silver has been used at the mint laboratory in Brussels, with gratifying results. Richards and Mueller[152] also view the method with favor. Potassium bromide (p. 252) is the most suitable standard substance. Obviously it must be free from chloride; preparation from recrystallized potassium bromate gives an excellent product.

(4) Ponndorf[153] applied his refined titration methods to the determination of silver with a standard chloride solution and was able to obtain results accurate to within 0.01%. In his procedure 5 ml. portions of the supernatant liquid are transferred to test tubes, to one of which is added 0.5 ml. of 0.001 N sodium chloride and to the other, 0.5 ml. of 0.001 N silver nitrate. The turbidities are compared and the end-point is considered to have been reached when they are alike. If there is a difference, the contents of the tubes are returned to the titration vessel (whereupon the added reagents neutralize each other) and the titration is continued. The principle is similar to that employed in *b*, the refinements consisting chiefly in the use of special volumetric apparatus and careful control of the temperature and other variables.

(*d*) ***Schneider Method:*** Palladium nitrate gives a red-brown precipitate of palladous iodide in the presence of iodide ions and may be used as an indicator for the titration of silver with a standard iodide solution. Schneider[154] prepares the indicator solution to contain 0.06 g. of palladium, as palladous nitrate, in 100 ml. of 16% nitric acid; 0.25 ml. of this in 10 ml. of water yields a detectable color with 0.007 mg. of iodide (0.7 mg. per liter, or approximately 5×10^{-6} M). When silver iodide is present the indicator is sensitive only to about 2 mg. of iodide per liter.

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[149] A. Levol, *Ann. chim. phys.*, **16**, 504 (1846). J. L. Gay-Lussac, *ibid.*, **17**, 232 (1846).

[150] J. S. Stas, *Compt. rend.*, **67**, 1107 (1868); *Ann. chim. phys.*, **25**, 22 (1872); *ibid.*, **3**, 145, 289 (1874).

[151] H. Beckurts, *Die Methoden der Massanalyse.* Vieweg, Braunschweig 1913, p. 868.

[152] T. W. Richards and E. Mueller, *J. Am. Chem. Soc.*, **29**, 652 (1907).

[153] W. Ponndorf, *Z. anal. Chem.*, **84**, 317 (1931).

[154] L. Schneider, *J. Am. Chem. Soc.*, **40**, 583 (1918).

Procedure: The sample is placed in a porcelain dish or square glass bottle and is treated with 0.5 ml. of indicator. While the liquid is stirred vigorously, the standard iodide solution is run in gradually. Near the end-point palladous iodide is coprecipitated and since it dissolves slowly the titration must be continued until the brown color remains even after 5 minutes of shaking. According to Schneider the addition of gum arabic as a protective colloid makes the procedure more rapid. A 5% solution, preserved with 0.1% thymol, is used; 5 ml. is taken in titrations with 0.1 N iodide or 1 ml. with 0.001 N. Gum arabic retards the flocculation of silver iodide so that the color change is visible throughout the entire volume.

Note: Schneider subtracts a correction of 0.03 ml. of 0.1 N solution and then finds the results to be accurate to within about 0.1%. With more dilute solutions the titration error is relatively much greater but the excess of standard solution required may be compensated for by the use of a reference solution. Within reasonable limits, colored salts do not interfere. Kolthoff obtained good results with 0.1 N solution but does not recommend the method for titrations of very dilute silver solutions. In preliminary experiments he found the reverse procedure useful for the determination of iodides; he did not investigate the possible interference of bromide or chloride.

CHAPTER IX

OTHER PRECIPITATION METHODS

1. Titrations with Ferrocyanide Solution; Determination of Zinc.— The first proposal that zinc should be determined volumetrically with ferrocyanide was made by Galletti,[1] who titrated an acetic acid solution of zinc at 40°C. until the mixture assumed a milky appearance. Fahlberg[2] chose to employ hydrochloric acid solutions and to use uranyl nitrate as an external indicator; the latter produces brown uranyl ferrocyanide in the presence of excess ferrocyanide. In order to coagulate the precipitate, Fahlberg added an excess of ammonium chloride.

A prolonged controversy over the composition of the precipitate was finally settled by the studies of de Koninck and Prost,[3] who established that a double salt is formed:

$$2K_4Fe(CN)_6 + 3Zn^{++} \rightleftarrows K_2Zn_3[Fe(CN)_6]_2 + 6K^+$$

The potassium zinc ferrocyanide is gelatinous when first precipitated and in this stage is capable of reacting with uranyl ions. It gradually changes to a powdery and less soluble modification of the same composition, however, and then is no longer reactive. Since the transition takes place more rapidly at higher temperatures, most workers recommend titrating a hot solution. De Koninck and Prost also suggested the addition of excess ferrocyanide to hasten the transition; the excess is titrated with a zinc solution after 15 minutes. This indirect method has not been widely adopted.

A superior procedure was proposed by Cone and Cady,[4] who recommended the internal indicators diphenylamine and diphenyl benzidine. These substances function as oxidation-reduction indicators (Vol. I, p. 133), being colored blue-violet by ferricyanide in acid solution. Addition of a trace of ferrocyanide lowers the oxidation potential enough to discharge the color. In the presence of zinc or certain other metals, the ferrocyanide is precipitated and the color is restored; the change is reversible.

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[1] M. Galletti, *Bull. soc. chim.*, II, **2**, 83 (1864), **9**, 369 (1868). *Cf. Z. anal. Chem.*, **4**, 213 (1865).

[2] C. Fahlberg, *Z. anal. Chem.*, **13**, 379 (1874).

[3] L. L. de Koninck and E. Prost, *Z. angew. Chem.*, **9**, 460, 564 (1896). The earlier literature is summarized in this paper and in H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig 1913, pp. 891–894.

[4] W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.*, **49**, 356 (1927).

The directions of Cone and Cady call for dissolving the sample, containing about 0.15 g. of zinc, in 15 ml. of 30% sulfuric acid, adding 100 ml. of water and 10 g. of ammonium chloride, and titrating with a ferrocyanide solution which contains a little ferricyanide. 4 to 6 drops of a 1% solution of diphenylbenzidine in strong sulfuric acid are added as indicator. During titration with ferrocyanide the blue color darkens, but changes to greenish yellow when the zinc has been precipitated. For best results Kolthoff found it necessary to work under somewhat modified and carefully controlled conditions.[5] Ammonium and sulfate ions are essential for a good color change, yet if the concentration of these is too high and the titration is carried out at room temperature, variations are obtained according to the rate of titration.

Kolthoff and Pearson[6] studied the method experimentally and proposed several modifications, taking into account the facts that the precipitate does not reach its theoretical composition immediately in a direct titration at room temperature and that a false endpoint may be observed. They prefer to employ a back-titration method, though the direct titration at 60°C. is satisfactory if more than 25 mg. of zinc is present.

Reagents: Potassium ferrocyanide solution, 0.025 M. Weigh out 10.557 g. of potassium ferrocyanide trihydrate, add 0.2 g. of sodium carbonate and dilute to one liter; keep in a dark bottle. To prepare the trihydrate, recrystallize a C.P. product from water and dry to constant weight over a solution saturated with sodium chloride and sucrose.

Potassium ferricyanide solution, 1%. Keep in a dark bottle and discard when more than 5 days old.

Zinc sulfate solution, 0.05 M. Dissolve 3.269 g. of pure zinc in an excess of dilute sulfuric acid and make up to one liter with water.

Indicator solution. Dissolve 1 g. of diphenylamine or diphenylbenzidine in 100 ml. of concentrated sulfuric acid.

Procedure I. Back-Titration at Room Temperature: The zinc solution is treated with enough sulfuric acid to make its concentration 0.5 to 1.5 N and ammonium sulfate to give a total of 0.5 to 1 g. per 50 ml. For this volume of liquid one adds 4 drops of ferricyanide solution and 2 drops of indicator, then ferrocyanide is run in moderately rapidly and with vigorous stirring until a 10 to 20% excess is present. After 2 minutes the excess is titrated with standard zinc solution to a change from yellow-green to blue-violet. Using diphenylamine the end-point may be perceived sharply, within one drop, but a correction of 0.035 ml. must be added to the volume of ferrocyanide consumed, for each drop of indicator taken. With diphenylbenzidine the change is less sharp but no correction need be applied. Results within 0.2% of the theoretical values can be obtained. 1 ml. of 0.025 M ferrocyanide corresponds to 2.45 mg. of zinc.

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[5] I. M. Kolthoff, *Chem. Weekblad*, **24**, 203 (1927).

[6] I. M. Kolthoff and E. A. Pearson, *Ind. Eng. Chem., Anal. Ed.*, **4**, 147 (1932).

Procedure II. Back-Titration at 60°C.: The conditions are the same as those of Procedure I, except that the solution is heated to about 60° immediately before addition of ferricyanide and indicator. The results are quite reproducible but tend to be from 0.5 to 1% low.

Procedure III. Direct Titration at 60°C.: This procedure is recommended only for titrations of more than 25 mg. of zinc in 50 ml. The solution is prepared as in Procedure I, warmed to 60°, treated with ferricyanide and indicator and titrated at once with ferrocyanide. Approximately 0.5 ml. before the end-point the color changes to yellow-green (false end-point), but after several seconds it reverts to blue-violet and the titration is then continued dropwise. At the final end-point the yellow-green color remains for at least 30 seconds. The change may be recognized to within a drop but the results average about 1% low even after correction for the indicator.

Notes: (1) Amounts of zinc as small as about 2 mg.may be titrated with an accuracy of 1–2% by Procedure I or II. For practical purposes it is generally convenient to standardize the ferrocyanide against a volume of zinc solution approximately equivalent to the quantity of zinc expected, regardless of which procedure is followed.

(2) Hydrochloric acid may be used in place of sulfuric if ammonium sulfate is also added. The end-point is somewhat sharper in sulfuric acid solution, however.

(3) Moderate amounts of alkali or alkaline earth salts (up to 1 g.) do not interfere. Not more than 50 mg. of aluminum should be present since it causes difficulty in recognition of the end-point. Preliminary separation of the zinc as sulfide is to be recommended in most cases.[7]

(4) Metals which form insoluble ferrocyanides, such as copper, cadmium, cobalt, nickel, and manganese, must be removed. Lead does not interfere since it is precipitated as sulfate under the specified conditions. Iron interferes markedly but amounts of less than 20 mg. may be rendered practically harmless by titration in the presence of excess potassium fluoride and hydrofluoric acid.

(5) Among other indicators which had been proposed for the zinc titration, prior to the introduction of diphenylbenzidine, are uranyl nitrate[8] (see p. 328), ferrous sulfate,[9] and alkali molybdate.[10] Molybdate gives a yellow color

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[7] *A.S.T.M. Methods of Chemical Analysis of Metals*, p. 151 (1943). H. A. Fales and G. M. Ware, *J. Am. Chem. Soc.*, **41**, 487 (1919). For the removal of cadmium with aluminum see F. E. Townsend and G. N. Cade, Jr., *Ind. Eng. Chem., Anal. Ed.*, **12**, 163 (1940).

[8] See also E. Murmann, *Z. anal. Chem.*, **45**, 174 (1906).

[9] W. W. Scott, *Chemical Methods for Analysis of Metallurgical Products.* 2nd ed., Van Nostrand, New York 1928, p. 643.

[10] H. Nissenson and W. Kettembeil, *Chem.-Ztg.*, **29**, 951 (1905).

with an excess of ferrocyanide but is not as satisfactory as the organic indicators.

Methyl red has been suggested[11] for the titration of a neutral zinc solution at 60°C. with ferrocyanide. Ammonium salts interfere and the method has little practical value. The color change is not reversible.

Tyler[12] recommends the use of *p*-ethoxychrysoidine (see p. 54, also Vol. I, p. 138) as indicator, particularly for the titration of zinc in rubber compounds after oxidation of the organic material with nitric acid, bromine, and, finally, perchloric acid. He notes that perchlorates have a detrimental effect upon the color change and position of the end-point when diphenylamine or diphenylbenzidine is employed, whereas these difficulties are not encountered with *p*-ethoxychrysoidine. Tyler's paper should be consulted for details of his procedure.

Frost[13] makes use of *o*-dianisidine as indicator but gives no experimental data concerning the accuracy or precision to be expected.

Determination of Indium: A procedure for the ferrocyanide titration of indium has been developed by Hope, Ross, and Skelley.[14] The indium solution should be brought to a concentration of at least 40% in acetic acid and should be free from chloride as well as from interfering metals. Two drops of 2% diphenylbenzidine indicator are added and the titration is made with a ferrocyanide solution containing 0.2% potassium ferricyanide. At the end-point the color changes from blue to green. The ferrocyanide is standardized against pure indium (evidently the composition of the precipitate has not been investigated).

Note: The indium solution may be freed from most interfering ions by precipitation of these with hydrogen sulfide in 1 N hydrochloric acid, followed by precipitation of the indium as hydroxide with ammonia and resolution in acetic acid. If ferric iron is present, 0.5 g. of potassium fluoride is added and the acetic acid concentration is brought up to 60%. Under these conditions the end-point is shown by a change from green to a blue which persists for at least 10 seconds.

Determination of Lead: Burstein[15] has suggested determining the strength of a lead solution by titrating a measured quantity of standard ferrocyanide with it (or by adding an excess of ferrocyanide and back-titrating with a known lead nitrate solution). 5 to 10 drops of 0.4% sodium alizarin sulfonate are added as indicator and the change is from yellow to red. It is probable that the p_H of the mixture has considerable influence on the result; Burstein apparently worked only with solutions of the salts as received.

Diphenylcarbazone as indicator is preferred by Ripan,[16] who titrates in the same direction as Burstein. To 10–15 ml. of 0.05 M ferrocyanide solution one adds an equal volume of water, 1 ml. of 0.3% diphenylcarbazone in alcohol, and enough saturated sodium acetate solution to give an orange-red color. This mixture is titrated with a neutral nitrate solution of the lead sample, made up to a definite volume such that the solution is approximately 0.1 M with respect to lead. The end-point is shown by a change to red. One ml. of 0.05 M potassium ferrocyanide is equivalent to 1 ml. of 0.1 M lead nitrate (20.72 mg. Pb).

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[11] I. Tananaew and M. Georgobiani, *Z. anal. Chem.*, **107**, 92 (1936).

[12] W. P. Tyler, *Ind. Eng. Chem., Anal. Ed.*, **14**, 114 (1942).

[13] H. H. Frost, *Analyst*, **68**, 51 (1943). The same compound has been employed as an indicator for oxidation-reduction titrations by M. E. Weeks, *Ind. Eng. Chem., Anal. Ed.*, **4**, 127 (1932).

[14] H. B. Hope, M. Ross, and J. F. Skelley, *Ind. Eng. Chem., Anal. Ed.*, **8**, 51 (1936).

[15] R. Burstein, *Z. anorg. allgem. Chem.*, **164**, 219 (1927).

[16] R. Ripan, *Z. anal. Chem.*, **123**, 251 (1942).

Determination of Ferrocyanide with Zinc Solution: The reverse titration of ferrocyanide with standard zinc sulfate or chloride solution (p. 302) may be employed for the assay of ferrocyanide preparations.[17] Potassium ferrocyanide reacts with zinc ions as shown by the equation on p. 301; if the sodium or lithium salt is being tested, sufficient potassium sulfate should be added to prevent the precipitation of zinc ferrocyanide, $Zn_2Fe(CN)_6$. If diphenylamine indicator and a little ferricyanide are added to an acidified ferrocyanide solution, the color remains yellow. During titration with standard zinc, white potassium zinc ferrocyanide is precipitated. The solution becomes somewhat greenish as the end-point is approached and finally changes sharply to a blue-violet.

Procedure: To 50 ml. of about 0.025 M potassium ferrocyanide solution are added 1 to 3 drops of 1% diphenylamine in concentrated sulfuric acid, 1 to 5 drops of 1% potassium ferricyanide solution and 10 to 20 ml. of 4 N sulfuric acid. This is titrated with a standard zinc solution added at a moderate rate at first but dropwise near the end-point. The color change may be recognized to within a drop but comes too soon, about 0.9% from the theoretical value; on this account it is advisable to standardize the zinc solution against pure potassium ferrocyanide.

Notes: (1) If an excess of zinc is added, it may be titrated back with standard ferrocyanide. An aqueous potassium ferrocyanide solution containing free carbonic acid is not stable; 0.2 to 1 g. of sodium carbonate should be added per liter.

(2) Lower results are obtained if large amounts of neutral salts are present. Substitution of hydrochloric acid for sulfuric also causes lower results, by about 1%. Diphenylbenzidine may be used as indicator in place of diphenylamine, but the color change is less sharp.

(3) Substances such as sulfide, thiosulfate, and thiocyanate, which might be present as impurities in crude ferrocyanides, interfere by reducing ferricyanide and destroying the indicator action. They may be oxidized by the addition of 2 to 4 ml. of 4 N sodium hydroxide and 10 ml. or more of 0.1 N bromine water, enough to give an odor of hypobromite. The excess, as well as the ferricyanide formed, is reduced by allowing the solution to stand with 10 ml. of

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[17] I. M. Kolthoff, *Chem. Weekblad,* **26,** 298 (1929).

0.1 N arsenous oxide until it has turned colorless or nearly so. The mixture is then treated with 4 N sulfuric acid and titrated as in the procedure above; the color change is not quite as distinct. Arsenous oxide reduces ferricyanide very slowly in acid medium but the reaction is quantitative within half an hour in alkaline solution.

Naturally any ferricyanide originally present is counted as ferrocyanide under these conditions. A mixture of ferro- and ferricyanide, free from reducing impurities, may be analyzed by this method. The ferrocyanide is titrated with zinc solution, then a duplicate sample is reduced with arsenite and the total is determined as ferrocyanide.

(4) Felkers[18] overcomes the interference of reducing substances by using the older spot method with ferric chloride as indicator. A portion of the solution must be filtered (or centrifuged) for each test. Since the sensitivity of the indicator is approximately 0.15 ml. of 0.05 M ferrocyanide in 100 ml. of solution, a correction of this magnitude has to be applied.

2. Direct and Reverse Titration of Sulfate with Barium Salt Solutions.—Various methods of determining sulfate or barium, generally indirect in the case of the former, have been described in preceding chapters. In this section are discussed the uses of sodium rhodizonate and tetrahydroxyquinone, two rather closely related compounds, as indicators. At the outset it may be mentioned that the volumetric determination of sulfate with barium, or vice versa, is no simple problem. The difficulties of coprecipitation and solubility which beset gravimetric methods[19] are likely to cause even greater disturbance in volumetric work. To these are added difficulties in the observation of the end-point. One can generally secure good results only through compensation of errors. The authors therefore regard the volumetric methods in general as suitable only for rapid control analyses. Nevertheless the practical importance of sulfate determinations is such that an attempt has been made to include here the essential details of several procedures described in the recent literature.

(*a*) ***Sodium Rhodizonate as Indicator:*** The use of sodium rhodizonate as an indicator for barium and sulfate titrations has been discussed thoroughly by Mutschin and Pollak.[20] The compound has the structure designated below as (I); it exists in two modifications, violet needles and lustrous octahedra. It is nearly insoluble in alcohol but dissolves in water to form an unstable yellow-brown solution. Decomposition to croconic acid occurs as the solution stands, or especially rapidly if it is warmed. According to Lerch[21] the barium salt may be either dark red or carmine red. Henle[22] stated that the formula of the barium salt is $C_6O_6Ba_2Cl_2 \cdot 4H_2O$ and that it has the structure shown in (II).

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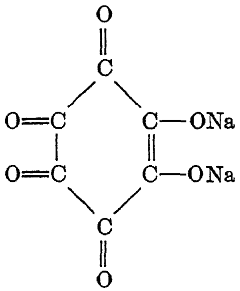
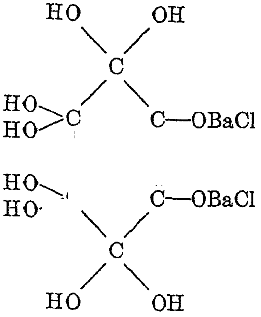
[18] P. F. Felkers, *Chem. Weekblad,* **27,** 209 (1930).

[19] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis,* Wiley, New York 1929, pp. 575–579. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis,* 2nd ed., Macmillan, New York 1943, pp. 329–339.

[20] A. Mutschin and R. Pollak, *Z. anal. Chem.,* **108,** 8 (1937).

(I)





(II)

Mutschin and Pollak found that the bluish red barium salt is formed only in the presence of chloride or other halide, thiocyanate or thiosulfate. In the absence of these ions a brownish red precipitate is formed.

The literature contains many references to the use of this indicator. Some authors secured useful results[23] while others found the method to be of questionable value.[24] According to Mutschin and Pollak the titration is impractical in acid solution but satisfactory results can be obtained in the titration of a neutral barium chloride solution containing acetone or an alcohol.

Procedure: The neutral sample, containing about the equivalent of 2 ml. of 0.2 N barium chloride, is treated with at least 2 g. of ammonium chlo-

[21] J. Lerch, *Ann.*, **124**, 20 (1862).

[22] F. Henle, *Ann.*, **350**, 330 (1906). *Cf.* F. Feigl and H. A. Suter, *Ind. Eng. Chem., Anal. Ed.*, **14**, 840 (1942).

[23] R. Strebinger and L. von Zombory, *Z. anal. Chem.*, **79**, 1 (1929); **105**, 346 (1936). P. N. Grigorjeff, *ibid.*, **94**, 251 (1933). M. Kefeli and E. Berliner, *ibid.*, **99**, 76 (1934). B. Paschke, *Z. Untersuch. Lebensm.*, **62**, 378 (1931); *Z. anal. Chem.*, **90**, 60 (1932). M. L. Tschepelevetszki and S. J. Posdniakov, *J. Chem. Ind. (U. S. S. R.)* **8**, 42 (1935); *Z. anal. Chem.*, **105**, 347 (1936).

[24] I. M. Kolthoff, *Pharm. Weekblad*, **62**, 1017 (1925). A. Friedrich and S. Rapoport, *Mikrochemie*, **14**, 41 (1934). M. G. Raeder, *Kgl. Norske Videnskab. Selskabs Forh.*, **5**, 32 (1932); *Chem. Abstracts*, **27**, 4499 (1933). J. C. Giblin, *Analyst*, **58**, 752 (1933). R. B. Roschal, *Chem. Abstracts*, **28**, 3688 (1934). W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 403 (1933), prefers tetrahydroxyquinone to sodium rhodizonate.

ride, 35 ml. of acetone (or methanol, ethanol, or propanol), and is diluted to 100 ml. with water. A saturated solution of the sodium rhodizonate is freshly prepared and from 1–1.5 ml. is added. The mixture is shaken and allowed to stand for a minute or two; after a bluish red color has developed one titrates with 0.2 N ammonium sulfate solution from a microburette. The additions are made at a rate of about one drop in 3 seconds until the color changes from blue to red, then more slowly and with vigorous shaking between drops. At the end-point there is a change from orange to yellow, which should be perceptible to within one drop.

Notes: (1) The direct titration of sulfate with barium does not give a good color change. Therefore in order to determine sulfate, more than enough barium chloride solution is added and the excess is titrated as described above. The solutions should be standardized empirically. Mutschin and Pollak[25] describe the determination of sulfate in the presence of various salts. Ammonium, sodium, and magnesium chlorides in concentrations of 1 or 2 g. per 100 ml. do not interfere, provided that the solutions are standardized under the same conditions. The same is true of potassium chloride, though in its presence the end-point is less sharp. A larger excess of barium chloride solution, 6 to 8 ml., is required if zinc or cadmium is present. Calcium sulfate is slightly soluble in acetone solutions, hence samples containing calcium should be treated with barium chloride before the acetone is added.

The titration fails if aluminum or phosphate is present. Ferric iron also interferes but may be removed by precipitation with ammonia and ammonium chloride. Nitrate should be expelled by evaporation with concentrated hydrochloric acid. Addition of formaldehyde prevents interference from sulfite.[26] Sulfide is not objectionable if the titration is made promptly or if glycerol is added to retard atmospheric oxidation of the sulfide. Thiosulfate interferes but may be converted to tetrathionate with iodine, the excess being reduced carefully with dilute thiosulfate solution. Perchlorate ions do not interfere in moderate concentrations.

(2) Abrahamczik and Blümel[27] modified the barium titration by incorporating the use of a citrate buffer ($p_H = 3$). The buffer solution is prepared from 7.00 g. of tertiary sodium citrate, 460 ml. of 0.1 N hydrochloric acid, and water to make 500 ml. 25 ml. of buffer is added to 10 ml. of approximately 0.1 N barium chloride and the mixture is diluted to 100 ml. To 3 ml. of this solution are added 10 ml. of methanol and 2 or 3 drops of 0.5% sodium rhodizonate indicator, freshly prepared. During titration with 0.01 N sulfate the reddish purple color fades to an orange, after which the reagent is introduced more slowly until only a faint bluish color remains. The end-point may be recognized sharply enough so that the error need not exceed 2%, according to these workers. They suggest filtration with sodium permutit as a means of removing interfering cations.

(3) The direct titration of sulfate with barium chloride, using sodium rhodizonate on filter paper as an external indicator, has also been recommended.[28] The sulfate solution, containing ammonium chloride and acetone as mentioned previously above, is shaken vigorously during the titration and drops are placed on filter paper freshly treated with indicator, until the first red color is obtained.

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[25] A. Mutschin and R. Pollak, *Z. anal. Chem.*, **108**, 309 (1937).

[26] A. Mutschin and R. Pollak, *Z. anal. Chem.*, **107**, 18 (1936).

[27] E. Abrahamczik and F. Blümel, *Mikrochim. Acta*, **1**, 354 (1937).

[28] J. C. Giblin, *Analyst*, **58**, 752 (1933). A. Mutschin and R. Pollak, *Z. anal. Chem.*, **106**, 385 (1936). G. V. Zararov, *Zavodskaya Lab.*, **8**, 933 (1939).

(4) Brunjes and Manning[29] report that sulfur in coal or coke can be determined volumetrically with rhodizonate after oxidation to sulfate according to the Eschka procedure. A stable indicator mixture is prepared by grinding 0.1 g. of sodium rhodizonate with 40 g. of ammonium chloride; 0.2 g. of the powder is used for each determination. The titration procedure is similar to that given above, with the exception that the solution is made to contain 50% ethanol by volume in place of acetone. An excess of from 3 to 5 ml. of 0.1 N barium chloride is added to the sulfate–alcohol solution. It should perhaps be noted that an error of 3 to 5% on the moderately small amount of sulfur present in coal is not considered excessive.

An improvement in the titration of barium, or of sulfate indirectly, has been developed by Miller.[30] A stable scarlet suspension of barium rhodizonate in ethanol serves as indicator. The procedure is quite rapid and results accurate to within about 1% are reported.

Preparation of Indicator: 40 mg. of sodium rhodizonate is dissolved in 20 ml. of water and a solution of 0.1 g. of barium chloride in a small amount of water is added. The brownish red precipitate is centrifuged and washed first with water and then with ethanol. To the precipitate one adds 5 ml. of ethanol containing 0.1 ml. of concentrated hydrochloric acid. The tube is placed in hot water for a few minutes, whereupon the complex is converted into its scarlet form. It is again centrifuged, decanted, and suspended at once in 250 ml. of ethanol. The suspension, which is stable for at least three months, should be kept in a glass-stoppered bottle and shaken well before each withdrawal.

Procedure for Sulfate Determination: The sample should contain from 2 to 20 mg. of sulfate and 0.5 to 1.0 ml. of 2 N hydrochloric acid, in 10 ml. of solution. It is heated to 90°C. and 0.02 M barium chloride is introduced, from a burette, at a rate of 1 ml. per minute until an excess is present. The excess should amount to 1 ml. with less than 10 mg. of sulfate present or to 2 ml. or more for larger quantities. The mixture is digested for 10 minutes at 90° and is cooled by immersion in cold water. Enough ethanol should be added so that it lacks 5 ml. of doubling the volume. The solution is titrated in the presence of 0.5 ml. of indicator suspension, with 0.02 M ammonium sulfate in 50% ethanol (by volume). A temperature of 25° should be maintained and the reagent should be introduced at a rate of one drop (0.015 ml.) in 10 seconds until the pink color disappears. Since the indicator suspension is unstable in the titration medium, the specified conditions must be followed closely.

Notes: (1) Interference is caused by calcium, lead, ferric iron, and phosphate (precipitation of barium phosphate). Ferric iron may be reduced with aluminum powder or with hydroxylamine hydrochloride. Apparently aluminum does not interfere in this procedure as greatly as in that of Mutschin and Pollak.

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[29] H. L. Brunjes and M. J. Manning, *Ind. Eng. Chem., Anal. Ed.*, **12,** 718 (1940). See also S. S. Tomkins, *ibid.*, **14,** 141 (1942).

[30] C. C. Miller, *J. Chem. Soc.*, **143,** 401 (1940).

(2) If preliminary neutralization of the sample is necessary, brilliant cresyl blue (Vol. I, p. 115) may be used as indicator. Hydrochloric acid is added until the blue color fades. The color returns upon the addition of ethanol but causes no difficulty with the end-point, which is from violet to pale blue under these conditions.

(3) A barium solution may be titrated directly as in the back-titration procedure given above. Miller also gives directions for the estimation of sulfur in pyrite by oxidation, precipitation, and titration.

(*b*) ***Tetrahydroxyquinone as Indicator:*** The use of the disodium salt of tetrahydroxyquinone as a qualitative test reagent for barium was suggested by Gutzeit.[31] The compound yields a red precipitate with barium ions. Schroeder[32] developed a procedure in which the formation of this red precipitate serves to indicate the end-point in a direct titration of a dilute sulfate solution with barium chloride. Since aqueous solutions of the indicator are not stable, Schroeder recommended that one part of the disodium salt be ground with 400 parts of dry potassium chloride and kept for subsequent use. The mixture is conveniently measured with a small cup or dipper capable of holding 0.2 g. This indicator powder, designated as THQ and commercialized by the Betz Laboratories, was used in most of the earlier studies. While many workers reported favorably concerning the method, a few[33] expressed dissatisfaction with it for certain applications in which they were interested. One difficulty may have been caused by the presence of potassium chloride introduced with the indicator; potassium ions are known to be occluded by barium sulfate. In 1938, Sheen and Kahler[34] noted that the indicator can be ground with an inert organic solid in place of potassium chloride, thus overcoming this disadvantage. Presumably the THQ mixture marketed since that time has been so prepared and the more recent literature data are based on the modified indicator.

The applicability of Schroeder's original procedure was widened by Sheen and Kahler[35] so that sulfate might be determined in solutions containing from 20 mg. to 30 g. per liter. In their studies with the potassium chloride–THQ indicator the titration was found to be accurate to within about 3%. The method is most useful for rapid technical determinations, such as in the analysis of boiler water. Some difficulty may be experienced with the end-point, which is not sharp to one unfamiliar with the color change.

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[31] G. Gutzeit, *Helv. Chim. Acta*, **12**, 727 (1929).

[32] W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 403 (1933).

[33] G. A. Ampt, *Australian Chem. Inst. J. & Proc.*, **2**, 10 (1935). D. T. Gibson and T. H. Caulfield, *Analyst*, **60**, 522 (1935). G. G. Manov and P. L. Kirk, *Ind. Eng. Chem., Anal. Ed.*, **9**, 198 (1937).

[34] R. T. Sheen and H. L. Kahler, *Ind. Eng. Chem., Anal. Ed.*, **10**, 206 (1938).

[35] R. T. Sheen and H. L. Kahler, *Ind. Eng. Chem., Anal. Ed.*, **8**, 127 (1936).

Procedure: 25 ml. of sulfate solution is adjusted with 0.02 N alkali or hydrochloric acid, to the point at which phenolphthalein becomes just colorless, and 25 ml. of ethyl or isopropyl alcohol is added. The solution is brought to 20–25°C., treated with the appropriate quantity of THQ powder as shown in the table below, and titrated with standard barium chloride of strength suited to the quantity of sulfate expected (see table). If more than 50 mg. of sulfate is present, sodium chloride is also added as noted in the table. The barium chloride is allowed to flow in at a steady but quite rapid rate of dropping and the mixture is shaken vigorously. The end-point is a change from yellow to pink throughout the entire solution.

CONDITIONS FOR TITRATION OF SULFATE WITH BARIUM CHLORIDE

Sulfate Present, *mg.*	THQ, *g.*	THQ, *dippers*	Sulfate Equivalent of Barium Chloride Solution, *mg. per ml.*	Sodium Chloride, *g.*
0 to 2.5[a]	0.1	0.5	1	0
2.5 to 25.0[a]	0.2	1	1	0
25.0 to 50.0	0.2	1	4	0
50.0 to 100.0	0.4	2	10	2
100.0 to 250.0	0.4	2	10	4
250.0 to 500.0	0.6	3	50	8
500.0 to 750.0	0.8	4	50	8

[a] A correction of 0.1 ml. of barium chloride solution should be subtracted.

Notes: (1) The end-point is observed most easily by looking horizontally through the suspension, which should be strongly illuminated from the side. Addition of more indicator in the titration of larger quantities of sulfate is made necessary by the fact that part of the indicator is coprecipitated.

(2) Phosphate interferes in the procedure as given. Up to 60 mg. of phosphate per liter (1.5 mg. $PO_4^{\equiv}$ per 25 ml.) may be tolerated if the solution is neutralized with 0.02 N hydrochloric acid to the yellow color of bromocresol green (p_H 4.0). If the bromocresol green color changes during titration, more acid should be added. Possibly a buffer of p_H 4.0 would be serviceable here.

(3) Not more than 5 mg. of ferric or ferrous iron, or aluminum, should be present in a liter of the water to be tested. These quantities are rarely encountered in natural waters. Silicate, chloride, and magnesium ions do not interfere. Up to 350 mg. of calcium per liter may be tolerated, but if more is present a precipitate of calcium sulfate is likely to form upon the addition of alcohol.

(4) The manufacturers of THQ[36] have suggested the addition of a small amount of silver nitrate to the solution before titration. The end-point can

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[36] W. H. and L. D. Betz, Philadelphia, Pa.

be perceived more clearly in the presence of the silver chloride which precipitates. 2 or 3 ml. of 0.1 N silver nitrate is taken for a volume of 50 ml. of alcohol–water solution.

(5) Numerous applications of the sulfate titration have been made to the determination of total sulfur in various products after oxidation by suitable methods. Gases may be burned in an atmosphere containing oxygen, the sulfur trioxide formed being caught in sodium carbonate solution and determined after neutralization.[37] Coal and coke are ignited in an oxygen bomb or by the Eschka method[38]; the oxygen bomb combustion is also applicable to the analysis of oils.[39] For the determination of sulfur in rubber, Sheen, Kahler, and Cline[40] oxidize the rubber by the same methods which would be employed in gravimetric analysis, then they precipitate sulfate with an excess of standard barium chloride solution. The suspension, containing free acid up to this point, is brought to the pink color of phenolphthalein with carbonate-free potassium hydroxide, in order to precipitate zinc, iron, and other metals. After filtration, excess barium in the neutralized filtrate is titrated with a standard sulfate solution and THQ indicator. The results check favorably with those obtained gravimetrically though in general they are a little higher, possibly because some barium is adsorbed by the hydrous oxide precipitate.

(6) The use of the sodium salt of tetrahydroxyquinone as an external indicator has been suggested by Lee and co-workers.[41] Filter paper is moistened in spots with a freshly prepared 10% solution of the sodium salt and the spots are treated with drops of the solution being titrated, until the end-point is shown by an immediate change (within 2 or 3 seconds) from yellow to pink. The color of a spot as much as 15 seconds old may be misleading. The chief advantage of the method is that very little tetrahydroxyquinone is required.

Applications to Semimicro Analysis: After a thorough study of the combustion of organic sulfur compounds and the microtitration of sulfate, Hallett and Kuipers[42] recommended the use of tetrahydroxyquinone as indicator in a rapid and fairly accurate method for the determination of sulfur.

Best results (within 1% of the theoretical) were obtained by burning the compound in oxygen as usual and collecting the combustion products in a special absorption apparatus including an electrical precipitator for sulfur trioxide mist. With such an apparatus no oxidizing agent is required in the absorbing solution. A simplified absorber can be utilized if an oxidant is added. Values accurate to within 2% were found when bromine was used and later expelled by heating; hydrogen peroxide was abandoned as an oxidant since it gave trouble with a fading end-point in the sulfate titration. The difficulty may have been caused by an inhibitor present in the peroxide, for destruction of the latter by prolonged boiling did not improve the end-point.

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[37] C. W. Wilson and W. A. Kemper, *Ind. Eng. Chem., Anal. Ed.*, **10**, 481 (1938).

[38] S. S. Tomkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 141 (1942). H. L. Brunjes and M. J. Manning, *ibid.*, **12**, 718 (1940).

[39] R. T. Sheen and H. L. Kahler, *Ind. Eng. Chem., Anal. Ed.*, **10**, 206 (1938).

[40] R. T. Sheen, H. L. Kahler, and D. C. Kline, *Ind. Eng. Chem., Anal. Ed.*, **9**, 69 (1937).

[41] S. W. Lee, J. H. Wallace, Jr., W. C. Hand, and N. B. Hannay, *Ind. Eng. Chem., Anal. Ed.*, **14**, 839 (1942).

[42] L. T. Hallett and J. W. Kuipers, *Ind. Eng. Chem., Anal. Ed.*, **12**, 357, 360 (1940).

The titration with 0.01 N barium chloride solution at a p_H of 6.5 to 7.0 was found to be satisfactory under conditions quite similar to those recommended by Sheen and Kahler (p. 311). For more exact location of the end-point, Hallett and Kuipers adopted a permanent color standard consisting of two layers of Wratten No. 21 light filter. Application of an indicator correction was found to be necessary, the correction after use of bromine as oxidant varying from −0.20 ml. with no sulfur to +0.25 ml. with 2.4 mg. In working with the electrical precipitator the corrections were from 0.04 to 0.10 ml. more negative, respectively. Theoretically one ml. of 0.01 N solution corresponds to 0.1603 mg. of sulfur.

Mahoney and Michell[43] made use of the THQ titration of sulfate after oxidizing organic sulfur by means of sodium peroxide–carbon fusion in an open nickel crucible.[44] Their titration method has been modified in some details by Jones,[45] who reports having obtained results accurate to within 1%. Jones oxidizes organic samples with a mixture of nitric and perchloric acids, then expels the nitric acid by boiling. A preliminary small scale oxidation should be performed on each sample to make sure that no explosion will occur.

Titration Procedure of Jones: The acid solution, containing from 2 to 6 mg. of sulfur in the form of sulfate and free from nitric acid or other interfering substances, is neutralized to phenolphthalein with ammonium hydroxide, boiled until colorless, and brought to a volume of 25 ml. Enough 0.05 N ammonium hydroxide is added to restore the pink color and this is followed by 2 ml. of saturated boric acid solution (if the pink color does not disappear, it is discharged by dropwise addition of 0.05 N perchloric acid). 25 ml. of 95% ethanol, 1 ml. of 10% ammonium chloride, and 0.15 g. of THQ are introduced and the solution is shaken and titrated slowly with 0.02 N barium chloride. About a milliliter or two before the expected end-point one adds 3 drops of 10% silver nitrate. The titration is continued dropwise, with thorough agitation, to a change from yellow to rose-pink throughout the solution.

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[43] J. F. Mahoney and J. H. Michell, *Ind. Eng. Chem., Anal. Ed.,* **14,** 97 (1942).

[44] G. G. Marvin and W. C. Schumb, *J. Am. Chem. Soc.,* **52,** 574 (1930). Presumably a Parr bomb procedure suitably modified from that described on p. 269 of this text might be used equally well; the alkali should be neutralized with hydrochloric acid instead of nitric. If gelatin capsules are used as containers for liquid samples, correction for the sulfur content of the gelatin is necessary.

[45] J. H. Jones, *J. Assoc. Official Agr. Chem.,* **26,** 182 (1943).

Note: Peabody and Fisher[46] recommend the use of a spot method in the titration of smaller volumes. The indicator solution is prepared by dissolving 0.15 g. of THQ in 1 ml. of water and 2 ml. of methyl cellosolve (2-methoxyethanol). In the standardization or analysis, 2 ml. of 0.1 N sulfate solution is treated with 2 ml. of ethanol and titrated with 0.1 N barium chloride. Near the end-point, drops are tested with indicator on a spot plate; the indicator becomes pink when a slight excess of barium is present.

(c) *Other Indicators for Sulfate Titrations with Barium Salts:* Methyl red has been found by Batchelder and Meloche[47] to show a color change from yellow to red during the titration of a neutral, carbon dioxide-free sulfate solution with barium chloride. The carbon dioxide may be eliminated either by performing the titration at boiling or by bubbling hydrogen through the solution. Apparently the color change is to be ascribed to a hydrolytic adsorption, the barium sulfate precipitate adsorbing barium ions and hydroxyl ions near the equivalence-point and thus leaving a trace of hydrochloric acid in solution. The method has little practical value since errors of about 3% are probable. Best results are obtained by titrating with a relatively concentrated barium chloride solution in a microburette.

Fluorescein has been proposed by Wellings[48] as an indicator for the titration of a neutral unbuffered sulfate solution with barium hydroxide in the presence of magnesium or manganese ions. Magnesium or manganese hydroxide is precipitated along with barium sulfate; at the end-point the hydroxide precipitate adsorbs fluorescein and changes color (yellow to pink or orange).

3. Titrations with Standard Lead Solutions.—Volumetric methods for several anions are based upon the formation of slightly soluble lead salts. In most of these methods the end-point is located with the aid of an adsorption indicator. Generally some preliminary practice is necessary before one can recognize the end-point definitely, hence it is advisable to experiment with known solutions, prepared from pure reagents or standardized gravimetrically, before titrating unknowns. Applications of the procedures are restricted since many anions and cations interfere and since the solutions must usually be neutral. Fortunately, better methods are available for most of the substances listed below.

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[46] W. A. Peabody and R. S. Fisher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 651 (1938). See also S. J. Kochor, *ibid.*, **9**, 331 (1937).

[47] G. Batchelder and V. W. Meloche, *J. Am. Chem. Soc.*, **54**, 1320 (1932).

[48] A. W. Wellings, *Trans. Faraday Soc.*, **28**, 561 (1932). The action of the indicator has been discussed by M. P. V. Iyer, *J. Indian Chem. Soc.*, **12**, 164 (1935).

Determination of Sulfate: According to Ricci,[49] eosin Y can be used as an indicator for the titration of sulfate with lead nitrate solution. From 0.1 to 0.15 g. of sulfate is dissolved in 15 ml. of water in a 250 ml. Erlenmeyer flask, neutralized if necessary, and treated with 12 drops of 0.5% eosin sodium salt in water. The titration with 0.1 M lead nitrate is carried out dropwise with vigorous shaking; a color change from yellow to red marks the end-point. The total volume at the end should be 30 ml. Ricci reports errors ranging from −0.5 to +0.7% on individual determinations, with no interference caused by the presence of up to 1 g. of alkali nitrate or chlorate. The use of a reference solution is advisable. Alcohol in small amounts has very little effect, but large quantities interfere with the end-point.

Burg[50] makes use of erythrosin B as indicator. The sample containing 0.05 to 0.19 g. of sulfate is diluted to a volume of 50 ml. in a 250 ml. flask, made alkaline to phenolphthalein and brought just to colorless with 0.02 N nitric acid. 16 ml. of alcohol and 14 drops of 1% erythrosin B (aqueous) are added and the temperature is adjusted to below 30°C. While the flask is swirled, 0.1 M lead nitrate is run in at a steady dropping rate until increasing persistence of the transient violet color indicates approach of the end-point. The titration is then continued more slowly until the color becomes a distinct violet. Final volume of the solution should not exceed 70 ml. Errors of ±0.4% are reported. Chloride interferes but may be titrated first with silver nitrate and dichlorofluorescein.

Determination of Phosphate: In this procedure, developed by Wellings,[51] a sample containing 0.06–0.12 g. of phosphate ion is adjusted with dilute alkali and nitric acid until colorless to phenolphthalein and is brought to a volume of about 25 ml. A 0.1% solution of dibromofluorescein in alcohol serves as indicator; 3 or 4 drops are added, whereupon the solution exhibits a fluorescent orange color. During titration with 0.05 M lead acetate the mixture is shaken vigorously. Lead phosphate, $Pb_3(PO_4)_2$, precipitates and at the end-point it assumes a permanent pink color. The titration is said to be accurate to within about 0.5% and to be applicable also to 0.005 M phosphate solutions. In the latter case only 1 or 2 drops of indicator are added.

Determination of Oxalate: Wellings[52] makes use of fluorescein in the titration of neutral oxalate solutions with 0.1 M lead acetate. 5 drops of 0.2% fluorescein in alcohol are taken for 20–50 ml. of oxalate solution. As the end-point is approached, the state of aggregation of the precipitate changes;

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[49] J. E. Ricci, *Ind. Eng. Chem., Anal. Ed.*, **8**, 130 (1936).

[50] W. V. Burg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 28 (1939).

[51] A. W. Wellings, *Analyst*, **60**, 316 (1935). *Cf.* Note (2), p. 317.

[52] A. W. Wellings, *Trans. Faraday Soc.*, **28**, 565 (1932).

when it is reached, the precipitate becomes pink. Errors of 0.3 to 1% are reported, the results generally being higher than those found by the permanganate method. No satisfactory color change occurs in the reverse titration.

Determination of Molybdate: Eosin A has been proposed[53] as indicator for the titration of molybdate with lead nitrate. The molybdate solution is adjusted to an acidity of 5×10^{-4} N with nitric acid and treated with a few drops of 0.5% sodium eosinate in water. At the end-point the color of the precipitated lead molybdate changes from a pinkish yellow to a rose red. The color change is reversible.

Determination of Tungstate: Diamine fast scarlet and diamine azo scarlet (British Colour Index Nos. 321 and 322) are reported to be suitable indicators.[54] The tungstate solution, which must be neutral, is brought to a volume of 20 ml., heated to boiling, treated with 5 drops of 0.1% indicator solution, and titrated with 0.1 or 0.01 N lead nitrate. During titration the solution is pink and the precipitate white; at the end-point the precipitate becomes pink and the solution colorless. The mixture should be heated and titrated further if necessary. It is stated that the error need not exceed 0.5% and that the presence of up to 2 g. of sodium or potassium chloride is not objectionable.

Ferrocyanide may be titrated with a lead nitrate solution according to the procedure given on p. 304. Determinations of a number of other anions are possible by the method of Evans, outlined below.

Titration of Lead with Various Reagents; (a) With Phosphoric Acid: A partially oxidized solution of diphenylcarbazide serves as indicator in a procedure developed by Evans[55] for the titration of small quantities of lead.

Indicator Solution: To 120 ml. of water add 2 ml. of approximately 6 N nitric acid (sp. gr. 1.2) and 30 ml. of pure pyridine, distilled over lead nitrate if necessary. To the mixture add 10 ml. of a 1.5% solution of diphenylcarbazide in alcohol and allow to stand overnight. This indicator solution is unstable and should be prepared freshly every few days. Some oxidation of the carbazide appears to be necessary.

If 10 ml. of indicator solution is added to 100 ml. of a neutral solution containing 1 mg. of lead, a cherry red color is produced; a blank without lead is a pale orange-brown. Upon addition of acetone the difference in color becomes more pronounced.

Procedure: The sample is adjusted so that from 1–20 mg. of lead is present in 100 ml. of neutral solution. To this are added 10 ml. of indicator and 30 ml. of acetone. A comparison blank of water, indicator, and acetone should also be prepared. The sample is titrated with approximately 0.001 M phosphoric acid until the color after the precipitate has settled matches that of the blank. Early in the titration the color diminishes rapidly but the change becomes much more gradual as the end-point is approached, especially during addition of the last 0.4 ml.

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[53] C. Cândea and I. G. Murgulescu, *Ann. chim. anal. chim. appl.*, **18**, 33 (1936); through *Chem. Abstracts*, **30**, 2133 (1936). *Cf.* Note (2), p. 317.

[54] Z. Raichinstein and N. Korobov, *Z. anal. Chem.*, **104**, 192 (1936).

[55] B. S. Evans, *Analyst*, **64**, 2 (1939).

The phosphoric acid is standardized against a known lead nitrate solution. Errors of up to 0.12 mg. of lead are possible, but they are usually not more than about 0.07 mg., according to Evans. The precipitate is said to have the composition $PbO[Pb_3(PO_4)_2]_2$.

Notes: (1) The titration may also be made with an ammonium vanadate solution.

(2) The reverse titration may be used for determining phosphate and other anions which yield slightly soluble lead salts. Evans applied the reverse method without modification to the titration of arsenate and vanadate. In the latter case, vanadate gives a color with the indicator but this fades during titration before the lead color appears. To determine molybdate, Evans substitutes an equal volume of alcohol for the acetone. Tungstate is titrated in the same way as phosphate, but with the addition of 2 ml. of saturated boric acid solution.

(3) Many cations interfere by forming colored compounds with the indicator. Thus it was found possible to titrate traces of zinc (0.1 to 1.0 mg.) with dilute ferrocyanide using diphenylcarbazide. The end-point corresponds to precipitation of the zinc as $Zn_2Fe(CN)_6$.

Tests carried out by the junior author have shown that Evans' method can be simplified considerably. Diphenylcarbazone serves as the indicator and is stable indefinitely in alcoholic solution; the pyridine acts mainly as a buffering agent and as such may with advantage be added separately from the indicator.

Reagents: Pyridine buffer. Dilute 30 ml. of redistilled pyridine with 120 ml. of water and add 2 ml. of 6 N nitric acid (1.55 ml. of 1:1 acid).

Standard phosphate solution, 0.001 M. Dissolve 0.1361 g. of analytical reagent potassium dihydrogen phosphate in water and dilute to one liter.

Standard lead solution, 0.100 mg. of lead per ml. Dissolve 0.100 g. of test lead in 10 ml. of water and 5 ml. of concentrated nitric acid, in a 150 ml. beaker. Evaporate to about 1 ml. and dilute to one liter with water.

Indicator solution. Dissolve 0.3 g. of "symmetrical diphenylcarbazone" in 100 ml. of 95% ethanol.

Procedure: Prepare the sample to be analyzed so that from 1 to 5 mg. of lead is present as the nitrate in a solution free from interfering substances. Adjust with diluted nitric acid or alkali to a p_H of about 3 (spot test with indicator paper) and bring the total volume to 50 ml. In the following order add 5 ml. of pyridine buffer, 1 ml. of indicator, and 15 ml. of redistilled acetone. Titrate with standard phosphate solution until the pink color is completely transformed to a pale yellow. The color fades gradually during the entire titration and the end-point is not sharp. It may be recognized most easily by titrating two identical samples; the first is brought to an approximate end-point and is treated with about 0.5 ml. of phosphate solution in excess, then the second is titrated to the point at which it just matches the first. Excess phosphate does not affect the yellow color after the pink has been discharged.

Standardize the phosphate against 25 ml. portions of standard lead solution (2.50 mg. of lead) diluted to 50 ml. and treated in exactly the same way as the sample. 1 ml. of 0.001 M phosphate corresponds to approximately 0.35 mg. of lead.

Notes: (1) The appearance of the end-point varies a little depending upon the quantity of lead present. With larger amounts, a precipitate of basic lead phosphate forms.

(2) Interference is caused by metals such as nickel, cobalt, zinc, and cadmium which react with the indicator, those such as aluminum and bismuth which consume phosphate, and by sulfate, arsenate, chromate, etc., which react with lead. Small amounts only of chloride, acetate, magnesium, or manganese may be tolerated but a fairly large quantity of alkali nitrate may be present.

(3) The determination of larger quantities of lead with 0.1 M disodium phosphate and various other reagents, in the presence of diphenylcarbazone as indicator, was studied by Ripan,[56] who titrates in the reverse direction. Under these conditions 10 ml. of 0.1 M phosphate is said to correspond to 15.00 to 15.07 ml. of 0.1 M lead. Ripan recommends the use of ferrocyanide in preference to phosphate or other reagents (see p. 304).

(*b*) ***With Molybdate:*** Henkel[57] tested the usefulness of several dyes as adsorption indicators. Those which he recommends are erythrosin (AGZ), Sirius red BB, Sirius violet 3B, fast red A, and benzo fast scarlet 4BA. The last two are Nos. 176 and 327, respectively, in the British Colour Index, while the Sirius dyes are products of the I. G. Farbenindustrie. 2 drops of 0.5% solution are used per 100 ml. of solution. With Sirius violet the precipitate remains colorless until the end-point is reached, whereas with the other indicators the precipitate changes from one color to another.

Eosin may also be used as indicator (*cf.* p. 316).

Errors in the determination of lead with molybdate are attributed by Holness[58] to improper initial neutralization of the lead solution and to the use of ammonium molybdate reagent, which produces an acid reaction. He therefore titrates with magnesium molybdate after neutralizing the solution to a p_H between 2 and 5.5. Too much acid interferes with the indicator change, but some must be present to prevent hydrolysis of the lead salt.

[56] R. Ripan, *Z. anal. Chem.*, **123**, 251 (1942).

[57] H. Henkel, *Z. anal. Chem.*, **119**, 326 (1940).

[58] H. Holness, *Analyst*, **69**, 145 (1944).

Magnesium molybdate reagent: Weigh out 14.4 g. of molybdic oxide and suspend in hot water. Add small quantities of magnesium carbonate (dense form) until there is no further evolution of carbon dioxide. Boil, filter, cool, and dilute to one liter. Standardize gravimetrically by conversion to lead molybdate, or volumetrically against a known lead solution, as in the procedure.

Solochrome Red B indicator: Prepare a 0.2% aqueous solution of the sodium salt of the *o*-carboxylic acid of benzeneazo-β-naphthol-3,6-disulfonic acid (British Colour Index No. 216).

Procedure: Weigh out a sample containing 0.1 to 0.9 g. of lead, dissolve in dilute nitric acid, and evaporate on a low heat hot plate (150°C.) until no more fumes are given off. Dissolve the lead nitrate in water, add 1–2 ml. of 0.01 M nitric acid and 4–5 drops of indicator solution, heat, and titrate with magnesium molybdate reagent. The end-point is a change in the solution from colorless to orange-red and on the precipitate from bluish pink to white. One may also titrate cold to a change from bluish pink to orange-red.

Notes: (1) The indicator behaves as an adsorption indicator and the color change is reversible. According to Holness the error does not exceed 0.2% in the titration of a hot solution.

(2) Tin forms stannic oxide which occludes some lead. In its presence one should boil the residue with water, add an excess of molybdate reagent, boil 5 to 10 minutes, make to volume, filter or allow to settle, and titrate an aliquot portion with 0.05 M lead nitrate solution. Antimony also interferes and no method was found for overcoming the interference.

(*c*) ***With Chromate:*** Lead solutions may be titrated with chromate using a few drops of 0.1% orthochrome T as indicator.[59] The change is from colorless to red in the solution. Probably orthochrome T acts as an acid-base indicator rather than as an adsorption indicator, so that this is an example of a hydrolytic precipitation method (p. 203).

The use of 2,6-dichlorophenolindophenol as an adsorption indicator is recommended by Fricke and Sammet,[60] who have developed procedures for the titration of macro and semimicro quantities of lead.

Macro titration: Prepare the lead sample so that about 20 ml. of 0.1 M lead nitrate is present in a solution not over 0.02 N in nitric acid. Add 10 drops of 0.2% indicator (freshly prepared aqueous solution) and titrate with 0.1 N potassium chromate, swirling well. Near the end a green color appears where each drop strikes, but disappears on mixing; later the entire solution becomes greenish but reverts to orange after vigorous shaking. At the end-point the green color remains. The observations may be checked by allowing the precipitate to settle: before the end-point the solution is pink, at the end, green, and afterwards, blue. The color changes are reversible. If salts such as potassium nitrate are present, one should use 20 drops of indicator and titrate to a more violet color.

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[59] H. McColloch Weir, *Dissertation,* Munich 1926.

[60] R. Fricke and R. Sammet, *Z. anal. Chem.*, **126,** 13 (1943).

The mean error is about 0.5% and the maximum error not more than 1%, according to Fricke and Sammet.

Semimicro titration: To about 20 mg. of lead as nitrate or bromide, in 30 ml. of water, add 20 drops of 0.02% indicator solution and titrate with 0.04 N potassium chromate. The violet color changes first to gray, then to orange. At the equivalence-point the precipitate coagulates and the solution becomes green. An error of up to 1.2% may be expected.

(*d*) ***With an Alkali Hydroxide or Carbonate:*** Wellings[61] made use of fluorescein (or its dichloro or dibromo derivative) as an adsorption indicator. The neutralized sample of lead as nitrate or acetate is made to a known volume and run from a burette into a standard solution of sodium hydroxide to which have been added a few drops of 0.1% fluorescein in alcohol. The precipitate turns pink at the end-point.

Roy[62] modified the procedure by pipetting the neutral lead solution into a slight excess of standard sodium carbonate and titrating back with standard lead nitrate, 0.02 to 0.05 N. Errors of the magnitude of 1% are probable.

(*e*) ***With Ferrocyanide:*** Sodium alizarin sulfonate and diphenylcarbazone may be used as indicators (see p. 304).

4. Titration of Fluoride with Thorium or Zirconium Solution.— Fluorine forms slightly soluble compounds or fairly stable complexes with a number of elements, including boron, silicon, titanium, thorium, zirconium, iron, aluminum, alkaline earths, magnesium, lead, and the rare earths (see p. 199). The reactions with thorium and zirconium, particularly the former, have been of considerable importance in the development of volumetric methods for the determination of fluoride. In view of the physiological effects of fluorine compounds, small quantities must frequently be determined in water and soils, or in foods which may have been treated with fluorine-bearing insecticides. Fluorine as a macro component may be encountered in the analysis of minerals, electrolytic cell bath materials and fluxes, insecticides, certain catalytic agents, and organic fluorides. Since the titration methods are subject to interference from a number of substances, preliminary separations are generally necessary. Distillation as hydrofluosilicic acid, as described later in this section, is the most commonly employed separation method.

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[61] A. W. Wellings, *Analyst*, **58**, 332 (1933).

[62] S. N. Roy, *J. Indian Chem. Soc.*, **13**, 40 (1936); *Chem. Abstracts*, **30**, 3740 (1936).

(*a*) ***Titration with Thorium Nitrate Solution:*** Willard and Winter[63] introduced a procedure in which a lake of zirconium and alizarin red serves as indicator for the titration of fluoride with thorium nitrate, in the presence of 50% ethyl alcohol. So long as fluoride is in excess, it binds the zirconium and the lake color does not appear. Armstrong[64] modified the method by omitting the use of a zirconium salt, since thorium is also capable of forming a lake with alizarin red. Other workers have confirmed the usefulness of his procedure. The p_H of the solution should be controlled carefully. According to Hoskins and Ferris[65] the optimum p_H is approximately 3.5 in 50% ethanol. They recommend that an equimolar solution of monochloroacetic acid and sodium monochloroacetate be added in an amount sufficient to make the buffer concentration 0.02 M. Armstrong later found[66] that the color change is sharper in aqueous medium than in alcoholic solution. Rowley and Churchill[67] came to the same conclusion concerning the titration of macro quantities of fluorine. In aqueous solution the p_H should be adjusted to between 2.9 and 3.2.

Reagents for Fluoride Determinations:

Standard fluoride solution, 2.210 g. of pure sodium fluoride per liter. 1 ml. contains one mg. of fluorine.

Thorium nitrate solution, approximately 0.1 N (13.8 g. of thorium nitrate tetrahydrate per liter). Standardize against the fluoride solution according to the procedure used in analyzing samples. These solutions are of the strength suitable for macro work and should be diluted by factors of 10, 100, or 250 for semimicro or micro titrations. Very weak fluoride solutions should be kept in paraffined bottles.

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[63] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933); O. B. Winter, *J. Assoc. Official Agr. Chem.*, **15**, 505 (1932).

[64] W. D. Armstrong, *J. Am. Chem. Soc.*, **55**, 1741 (1933).

[65] W. M. Hoskins and C. A. Ferris, *Ind. Eng. Chem., Anal. Ed.*, **8**, 6 (1936). *Cf.* J. N. Frers and H. Lauckner, *Z. anal. Chem.*, **110**, 251 (1937); J. F. McClendon and W. C. Foster, *Ind. Eng. Chem., Anal. Ed.*, **13**, 280 (1941); M. P. Matuszak and D. R. Brown, *ibid.*, **17**, 100 (1945).

[66] W. D. Armstrong, *Ind. Eng. Chem., Anal. Ed.*, **8**, 384 (1936). H. C. Lockwood, *Analyst*, **62**, 775 (1937), prefers to use glycerin in place of alcohol.

[67] R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).

Buffer, 9.45 g. of monochloroacetic acid and 2.00 g. of sodium hydroxide dissolved in 100 ml. of water.

Indicator, 0.05 g. of sodium alizarin sulfonate dissolved in 100 ml. of water.

Procedure of Rowley and Churchill[67] *for Macro Titration:* Prepare the sample so that from 1–50 mg. of fluorine is present in 100 ml. of solution. Add 8 drops of indicator solution and neutralize by adjusting with 2% sodium hydroxide and 1:200 hydrochloric acid until the solution is just acid (pink color discharged). Add 1 ml. of chloroacetate buffer and titrate with 0.1 N thorium nitrate to a permanent pink color. Carry out a blank determination also and subtract it from the sample titration.

Notes: (1) Interference is caused by any substance capable of forming a slightly soluble compound or stable complex with fluoride or thorium. These include sulfate, arsenate, phosphate, organic anions, and excessive amounts of halides or nitrate, in addition to many of the ions mentioned on p. 320. If the fluoride is isolated by distillation as hydrofluosilicic acid, it is well to standardize the thorium nitrate solution against a known quantity of fluoride which has been distilled in a similar way.

(2) Working with pure fluoride solutions (1 to 50 mg. of fluorine), Rowley and Churchill obtained results lying generally within 0.1 mg. of the theoretical values. The equivalence of the thorium and fluoride solutions was maintained over the entire range and the end-point was found to be quite definite. On the other hand, Reynolds and Hill[68] reported that there is a small titration blank which increases noticeably with dilution.

Procedure of Armstrong[66] *for Micro Titration:* Prepare the sample so that from 1 to 10 μg. of fluorine is present in 1 ml. of solution, free from interfering substances. To each of several one ml. portions add 1 drop of indicator and sufficient 0.03 N hydrochloric acid (in split drops) to bring the solution to a light orange color. Add 1 drop of buffer and titrate with 0.0004 N thorium nitrate to the first perceptible pink color. Read the microburette to the nearest 0.005 ml. Standardize the thorium solution by titrating knowns containing 1 and 10 μg. of fluorine, under the same conditions. Subtract the lower titration from the higher to obtain a corrected titer for 9 μg., from which the equivalence of the solutions may be calculated. One-ninth of the difference gives the corrected titer for 1 μg., the discrepancy between this and the observed titer being the titration blank of thorium required to produce a pink color. All of the solutions must be titrated to the same appearance, one serving as a reference for the others.

[68] D. S. Reynolds and W. L. Hill, *Ind. Eng. Chem., Anal. Ed.,* **11,** 21 (1939).

Notes: (1) Armstrong reported good results (−0.8 to −2.0% error) based upon the means of four analyses from each distilled solution. McClure[69] was unable to secure such good accuracy in individual determinations; he recommended that at least 5 μg. of fluorine be titrated in order to diminish the effect of any error in the blank correction. McClendon and Foster[55] obtained recoveries ranging from −2 to +7%, generally high, in the titration of from 1 to 10 μg. They titrate the fluoride solutions in 100 ml. Nessler tubes viewed against a white table top, with illumination from a 20 watt fluorescent lamp 6 inches above the table. It is probable that the errors reported occur in large part as a result of distillation; in any case they are not surprising when one considers the small magnitude of the quantities sought.

(2) Dahle, Bonnar, and Wichmann[70] observed that relatively small amounts of sodium in the form of chloride or perchlorate introduce a significant error in the titration. The use of a buffer or of dilute sodium hydroxide to neutralize free acidity, such as that from acid carried over during distillation, is therefore objectionable. To avoid the difficulty they recommend a "back-titration" method suggested to them in a private communication from W. S. Allen. The procedure given below combines directions of these workers with modifications introduced by Clifford.[71]

Back-Titration Procedure: Titrate one aliquot portion of the slightly acid fluoride solution (distillate) with 0.05 N sodium hydroxide, to alizarin red S. From this titration calculate how much 0.05 N hydrochloric or perchloric acid must be added to an equal portion in order to make the total acidity equivalent to 2.0 ml. of 0.05 N. Add the calculated quantity of acid to the duplicate portion in a 50 ml. Nessler tube and dilute to approximately 40 ml. with water. Introduce 1.0 ml. of 0.01% sodium alizarin sulfonate solution, titrate with 0.0004 N thorium nitrate to a "tannish pink" color, and bring to a volume of 50 ml.

Prepare a blank with distilled water, 2.0 ml. of 0.05 N acid, indicator, and as much thorium nitrate as was added to the sample. Now titrate the blank with standard fluoride solution (0.01 mg. fluoride per ml.) until its color matches that of the unknown. This final titration is a direct measure of the fluoride in the sample aliquot.

Notes: (1) The end-point is not sharp. There is a gradual change from yellow to pink; any intermediate point may be selected so long as the colors of sample and blank are matched carefully under identical conditions. Mixing is best accomplished by pouring from the Nessler tube into a beaker and back, after each addition of reagent.

(2) In titrations of from 0.5 to 12 μg. of fluorine in pure undistilled solutions, Clifford[72] observed a very slight positive error (0.1 μg.). In the higher range, up to 75 μg., the errors ranged from −1 to −2 μg.

(3) Clifford has suggested the use of potassium fluosilicate in place of fluoride for the standard solution. Inasmuch as a fluoride distillate contains the equivalent quantity of silicate, this appears to be a worthwhile suggestion.

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[69] F. J. McClure, *Ind. Eng. Chem., Anal. Ed.*, **11**, 171 (1939).

[70] D. Dahle, R. U. Bonnar, and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **21**, 459, 468 (1938).

[71] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **23**, 303 (1940); **24**, 350, 356 (1941); **27**, 90, 246 (1944).

[72] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **25**, 396 (1942).

Removal of Interfering Substances: Willard and Winter[73] studied various methods for separating fluorine from other substances and concluded that volatilization as hydrofluosilicic acid gives the best results. Their method, with slight modifications, has been widely accepted. The sample, which should be free from or very low in organic matter, (see Note 3 below), is placed in a small distilling flask along with a few glass beads, 5 ml. of 60% perchloric acid, and enough water so that the solution will boil at 110°C. or less. The flask is supported upon an asbestos mat with an opening large enough so that about one-third of the vessel is exposed to the flame. The flask may be closed with a rubber stopper, though an all-glass apparatus is preferable. In either case, the flask is provided with a thermometer and a dropping funnel (with capillary tubing), both dipping beneath the liquid. The distillate passes through a water condenser and is collected in a beaker or volumetric flask. Distillation is allowed to proceed until the boiling point reaches 135° and then is continued with addition of water through the dropping funnel to prevent the temperature from going appreciably higher. Usually all of the fluorine will have been volatilized when from 50–75 ml. of distillate has been collected, unless boric acid or gelatinous silica is present. These substances retard the distillation.

Before titration of fluoride, the distillate must be neutralized carefully or buffered (pp. 321, 323). If free chlorine may be present from decomposition of the perchloric acid, 1 ml. of 0.1% hydroxylamine hydrochloride solution should be added.[74]

Notes: (1) Modifications of the distillation apparatus have been described by various workers,[75] chiefly with the aims of making the method simpler or more suitable for the determination of very small quantities, and of preventing the entrainment of perchloric acid. Armstrong[66] reported that addition of sodium perchlorate to the still reduces the amount of perchloric acid carried over.

(2) Interference from chloride may be prevented by adding an excess of solid silver sulfate to the still, according to McClure.[76]

(3) Organic matter and other reducing agents interfere by decomposing perchloric acid. Reynolds and Hill[77] recommend the use of a saturated potassium permanganate solution to oxidize organic substances and pyritic sul-

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[73] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

[74] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **24**, 350 (1941). *Cf.* H. C. Lockwood, *Analyst*, **62**, 775 (1937).

[75] J. F. McClendon and W. C. Foster, *Ind. Eng. Chem., Anal. Ed.*, **13**, 280 (1941). W. H. Gilkey, H. L. Rohs, and H. V. Hansen, *ibid.*, **8**, 150 (1936). D. S. Reynolds, J. B. Kershaw, and K. D. Jacob, *J. Assoc. Official Agr. Chem.*, **19**, 156 (1936).

[76] F. J. McClure, *Ind. Eng. Chem., Anal. Ed.*, **11**, 171 (1939). *Cf.* W. F. Eberz, F. C. Lamb, and C. E. Lachele, *ibid.*, **10**, 259 (1938), and W. D. Armstrong, *ibid.*, **8**, 384 (1936), who employ a preliminary precipitation with silver perchlorate, not in excess.

[77] D. S. Reynolds and W. L. Hill, *Ind. Eng. Chem., Anal. Ed.*, **11**, 21 (1939).

fur. A correspondingly greater quantity of perchloric acid should also be added.

MacIntire and Hammond[78] destroy organic matter by igniting the sample in the presence of calcium or magnesium peroxide. Crutchfield[79] prefers to moisten the material with 5 ml. of 60% magnesium acetate tetrahydrate in water, before igniting. The magnesium acetate is prepared from pure magnesium to ensure freedom from fluoride. McClendon and Foster[75] reject ordinary ashing methods and employ a closed system with a platinum combustion tube, burning the sample in oxygen and recovering the vaporized hydrofluoric acid in an absorber.

(4) Willard and Winter[73] applied the perchloric acid distillation method directly to several insoluble fluorides (fluorite, apatite, rock phosphate, and cryolite) with satisfactory results. Substances such as opal glass must first be fused with sodium carbonate. Hoffman and Lundell[80] found the fusion treatment advisable also in the analysis of fluorite, somewhat low results being obtained otherwise. Samples which may contain reduction products from phosphates should be given a double distillation, according to Churchill and co-workers.[81] In the first step the solution is acidified with sulfuric acid and the distillate is made alkaline and evaporated. The second distillation is made with perchloric acid as usual.

(5) Clifford[82] made a thorough study of the microdistillation of fluoride. His refinements include the use of an all-glass still heated in a bath of Wood's metal which is kept at 180–200°C. in a shielded iron crucible. The level of the molten metal is kept just below that of the liquid in the flask. Perchloric acid is preboiled to remove fluoride, the 60% acid being diluted with 3 or 4 times its volume of water and concentrated to its original volume. 20 ml. is used for each determination. Between analyses the still is washed with hot 10% sodium hydroxide and water to remove any residual fluoride, then some sulfuric acid is heated to fumes in the flask in order to dehydrate silicic acid adhering to the walls. Even with these precautions Clifford found a blank of 0.9–1.0 μg. of fluorine in 150 ml. of distillate taken off at 135–140°. This evidently came from the Pyrex glass of the apparatus, which contained 0.02% fluorine.

It is very difficult to distill hydrofluosilicic acid quantitatively on a micro scale. Clifford obtained a recovery of 98.4% with 200 μg. of fluorine. Apparently the excellent results reported by some workers have been obtained through compensation of errors, losses being offset by a carry-over from one analysis to the next.

(*b*) ***Titration with Zirconium Oxychloride Solution:*** de Boer and Basart[83] based a rapid test for fluoride upon its bleaching of colored anthraquinone–zirconium complexes in strongly acid solution. An empirical titration method for fluoride, involving the same reaction, has been developed by Kolthoff and Stansby.[84]

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[78] W. H. MacIntire and J. W. Hammond, *J. Assoc. Official Agr. Chem.*, **22**, 231 (1939). For a double distillation method with intermediate ashing, for carbohydrate foods, see W. H. King and D. A. Luhorn, *Ind. Eng. Chem., Anal. Ed.*, **16**, 457 (1944).

[79] W. E. Crutchfield, Jr., *Ind. Eng. Chem., Anal. Ed.*, **14**, 57 (1942).

[80] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **20**, 607 (1938).

[81] H. V. Churchill, R. W. Bridges, and R. J. Rowley, *Ind. Eng. Chem., Anal. Ed.*, **9**, 222 (1937).

[82] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **24**, 350 (1941). *Cf.* D. Dahle, *ibid.*, **22**, 338 (1939). See also a report to the Analytical Methods Committee, Society of Public Analysts, *Analyst*, **69**, 243 (1944).

[83] J. H. de Boer and J. Basart, *Z. anorg. allgem. Chem.*, **152**, 213 (1926). J. H. de Boer, *Rec. trav. chim.*, **44**, 1071 (1925).

Reagents: Purpurin indicator, 0.300 g. of purpurin (1,2,4-trihydroxyanthraquinone) dissolved in one liter of ethyl alcohol.

Zirconium solution, 2.83 g. of zirconium oxychloride octahydrate, or enough to furnish 0.8 g. of zirconium, diluted to one liter with 10 N hydrochloric acid.

Hydrochloric acid, 10 N, prepared by adding 120 ml. of water to 880 ml. of concentrated acid.

Comparison solution, 19.60 g. of cobalt nitrate hexahydrate and 0.132 g. of potassium dichromate diluted to one liter with water.

Procedure: Place the sample, containing 0.5 to 15 mg. of fluoride, in a cylindrical oil-sample bottle of 100 ml. capacity and adjust with water or acid so that, altogether, 2 ml. of water and 5 ml. of 10 N hydrochloric acid are present. Add 2 ml. of purpurin solution, from a pipette. Into a similar bottle put 40 ml. of the comparison solution, measured from a graduate. Titrate the sample with zirconium solution until its color nears that of the comparison liquid, then add more 10 N hydrochloric acid to bring the total volume just under 40 ml. Finally complete the additions of zirconium and acid when the sample and comparison solution are alike in color and volume. The zirconium solution must be introduced slowly, with shaking.

Kolthoff and Stansby calculate the amount of fluoride present by subtracting 1 mg. from the quantity of zirconium used and reading the fluoride equivalent of the remainder from an empirical table, given in the original article. The correction is approximately twice that required for a blank, but is applied to compensate for excess "blank" zirconium required in the presence of fluoride (hydrolysis of the complex). Roughly expressed, each milligram of zirconium used (corrected) is equivalent to 0.40 mg. of fluoride when from 0.4 to 2 mg. are present, to 0.42 mg. with 5 mg. present, to 0.44 mg. with 8 mg. and to 0.48 mg. with 10 mg. present. The actual values should be determined for the particular reagents employed.

Notes: (1) Although the color change at the end-point is not sharp, it is possible to determine from 5 to 15 mg. of fluoride to within 1%. An error of 3 or 4% is probable in the titration of 1 mg. Kolthoff and Stansby have also worked out conditions for micro determinations; the details are given in their paper.

(2) The zirconium solution may become cloudy after several months. It should therefore be prepared freshly or restandardized frequently.

(3) Since this titration takes place in a strongly acid solution, it is somewhat less subject to interference than the thorium titration. However, difficulty is caused by the presence of colored compounds, oxidizing agents, and sub-

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[84] I. M. Kolthoff and M. E. Stansby, *Ind. Eng. Chem., Anal. Ed.*, **6**, 118 (1934).

stances which react with zirconium or fluoride. Therefore phosphate, borate sulfate, oxalate, nitrite, and aluminum must be removed if present. Use may be made of the Willard and Winter distillation method described previously, or of the distillation of fluorine as silicon tetrafluoride. Kolthoff and Stansby obtained good results with the latter; they studied also some chemical separation methods.

(4) The titration has been applied by Clifford[85] to the determination of fluoride in spray residues on fruits.

5. Titration of Chloride or Bromide with Mercurous Nitrate.— Mercurous mercury forms slightly soluble halide salts; methods similar to those of argentometry are therefore possible though of less practical importance. Adsorption indicators are generally employed.

Preparation of Reagent[86]*:* Take slightly more mercurous nitrate (analytical reagent grade) than is required to prepare a 0.1 N solution and triturate it in quantities of 2–3 g. with 50 ml. portions of water. Upon filtration and dilution to 0.1 N, the solution may be from 0.01 to 0.02 N in free nitric acid. Addition of a few drops of mercury serves to stabilize the reagent for at least 6 months; it should be standardized against a known halide solution in the way in which it is to be used.

Procedure: According to Burstein,[87] bromide can be titrated using sodium alizarin sulfonate as indicator. The color change is from red to violet. The reverse titration of mercurous ions with bromide is not feasible, but mercurous salts may be determined by adding an excess of bromide and back-titrating. Kolthoff found that the color change is not very distinct with 0.1 N solutions. The error in judging the end-point may amount to 0.1 to 0.2 ml. With 0.01 N solutions the color change is considerably better, since at this dilution mercurous bromide remains in a colloidal dispersion. Nevertheless the error amounts to from 0.5 to 1%.

Use of bromophenol blue or bromocresol purple as indicator is advocated by von Zombory.[88] The color change from yellow to lilac is more easily perceptible in the determination of bromide than in that of chloride. In the case of chloride, a violet shade appears somewhat early and becomes stronger at the end-point. The reverse titration, of mercurous ion with bromide, is said to be satisfactory with either indicator, while that with chloride is good only with bromophenol blue.

Chlorophenol red and bromocresol green have also been studied[89] but appear to offer no especial advantages. The color change, from yellow to violet, is not particularly sharp in the chloride titration. To determine mercurous ion, it is best to add an excess of standard bromide and back-titrate.

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[85] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **27**, 98, 254 (1944).

[86] I. M. Kolthoff and W. D. Larson, *J. Am. Chem. Soc.*, **56**, 1881 (1934).

[87] R. Burstein, *Z. anorg. allgem. Chem.*, **168**, 325 (1928).

[88] L. v. Zombory, *Z. anorg. allgem. Chem.*, **184**, 237 (1929).

[89] L. v. Zombory and L. Pollak, *ibid.*, **215**, 255 (1933).

Kolthoff and Larson[86] prefer bromophenol blue as indicator, using 4 to 6 drops of 0.1% solution for 25 ml. of 0.1 N chloride or bromide. The color change is distinct in either direction and the titration error is negligible. However, no sharp end-point is obtained with chloride solutions weaker than 0.04 N or bromide solutions weaker than 0.01 N. Nitric acid (up to 0.2 N) and sulfuric acid (up to 0.1 N) do not interfere, but greater concentrations make the end-point much less distinct. In the presence of acid the change is from yellow to gray rather than to violet. No interference is caused by the nitrates of aluminum, iron, calcium, barium, or alkalies. No more than 0.5 g. of potassium sulfate should be present in 25 ml., since larger quantities delay the end-point. The method is useless if even small amounts of copper, zinc, or cadmium are present.

Titration of Iodide with Mercuric Chloride Solution: According to Korenman[90] mercuric chloride serves as a reagent for the micro determination of iodide. To 3 ml. of about 0.01 N iodide solution (neutral or very weakly acid) one adds 1 ml. of 0.5% starch indicator and 3 drops of a 0.02% aqueous iodine solution. The titration is carried out with 0.001 M mercuric chloride from a microburette, until the solution becomes colorless (*cf.* p. 274). Korenman's procedure is also applicable to the micro determination of silver or mercury; the sample is diluted to known volume and added from a microburette to a standard iodide–starch–iodine mixture.

6. Titration of Phosphate with Uranyl Acetate.—The precipitation of phosphate with a uranyl salt, first employed for volumetric analytical purposes by Leconte,[91] was revived independently by Neubauer[92] and by Pincus.[93] Potassium ferrocyanide serves as an external indicator, giving a brown precipitate when uranyl ions are present in excess. In an ammonium acetate–acetic acid solution the insoluble phosphate formed is said to have the formula $UO_2NH_4PO_4$. The method is somewhat empirical, the result being influenced by the composition of the solution. Therefore the uranyl solution (preferably the acetate) should be standardized against a known quantity of phosphate under conditions similar to those prevailing in the analysis.

In removing drops for spot tests the solution taken should be clear, since any precipitate present will react with ferrocyanide and give a premature end-point. Good results can be obtained if, near the end-point, each small portion to be tested is first filtered or centrifuged. Without this precaution the results are not dependable.

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[90] I. M. Korenman, *Mikrochemie*, **14**, 181 (1934).

[91] C. Leconte, *Compt. rend.*, **29**, 55 (1849).

[92] C. Neubauer, 1858; quoted in H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig 1913, p. 950.

[93] Pincus, *J. prakt. Chem.*, **76**, 104 (1859). *Cf.* C. Schumann, *Z. anal. Chem.*, **11**, 388 (1872).

The method has been employed quite widely in physiological chemistry and for fertilizer analysis, but is not worthy of commendation. Interference is caused by any substance, such as iron or aluminum, which forms a phosphate insoluble in a buffered acetic acid solution.

Pyrophosphate in the Presence of Orthophosphate: Dworzak and Reich-Rohrwig[94] showed that pyrophosphate forms a soluble complex salt with uranyl acetate:

$$2Na_4P_2O_7 + UO_2(C_2H_3O_2)_2 \rightarrow Na_6UO_2(P_2O_7)_2 + 2NaC_2H_3O_2$$

If an excess of uranyl acetate is added, uranyl phosphate precipitates. To determine the exact end-point in a titration is difficult. One first makes a preliminary titration to the formation of a permanent turbidity. Then a series of replicate portions is set up with somewhere near the required quantity of uranyl solution, added in increments of 0.5 or 1.0 ml. such that the lowest remains clear while the highest eventually becomes distinctly turbid. Each portion is treated with 1 N ammonia, in an amount depending upon the quantity of uranyl reagent added (0.1 ml. for 10 ml., 0.5 ml. for 20 ml., 4 ml. for 50 ml.), and the mixtures are allowed to stand for at least 6 hours. The end-point is taken as an average of the volume of reagent added to the last clear portion and that added to the first slightly turbid portion.

The reagent is made up with 20 g. of uranyl acetate per liter and its uranium content is determined gravimetrically. 1 g. of uranium is said to be equivalent to 2.234 g. of tetrasodium pyrophosphate. At best the procedure is tedious and uncertain, so that other methods would be preferable (pp. 139, 141).

7. Titration of Copper with Thiocyanate.—In a method proposed by Boye,[95] cupric copper is reduced with hydroxylamine sulfate and titrated with thiocyanate in an inert atmosphere. The thiocyanate solution (0.5 N) is prepared in freshly boiled and cooled water. A ferric salt is used as indicator.

Procedure: Prepare the sample so that from 0.1–0.2 g. of copper is present in 75 ml. of solution, barely acid with sulfuric or hydrochloric acid. Add 25 ml. of methanol and heat to boiling, meanwhile displacing air by passing a stream of nitrogen or carbon dioxide into the vessel, just above the surface of the liquid. When the boiling point has been reached, add in small portions a total of 0.5–1 g. of hydroxylamine sulfate. After the mixture has become colorless, cool to 15–20°C., add one drop of saturated ferric ammonium sulfate solution, and titrate with thiocyanate to a light pink-amber color. Gas should be passed into the vessel continuously during cooling and titration.

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[94] R. Dworzak and W. Reich-Rohrwig, *Z. anal. Chem.*, **77**, 14 (1929).

[95] E. Boye, *Ber.*, **B67**, 1119 (1934).

One milliliter of 0.5 N thiocyanate is equivalent to 31.8 mg. of copper.

Note: The results tend to be from 0.1–0.3% low, possibly because of oxidation by the ferric indicator solution. The procedure is not well suited for the analysis of more dilute copper solutions.

Interference would be caused by substances which interfere in ordinary Volhard titrations (p. 262) as well as by oxidizing agents such as nitric acid.

CHAPTER X

FORMATION OF SLIGHTLY DISSOCIATED OR COMPLEX COMPOUNDS. MERCURIMETRY

1. Determination of Halides.—(*a*) ***Sodium Nitroprusside as Indicator:*** In contrast with the ions of most metals, those of divalent mercury form complex or slightly dissociated compounds with halogen ions and several other anions. This property may be utilized for the determination of mercury or of the anions in question. The reaction between divalent mercury and cyanide has already been mentioned in connection with acidimetric methods for these and other substances (pp. 204–208). In general, the dissociation constants of mercuric compounds decrease in the following order:

$$HgCl_2 > HgBr_2 > Hg(CNS)_2 > HgI_2 > Hg(CN)_2$$

If to a halide solution one adds a normally dissociated mercuric salt, such as the nitrate or perchlorate, halide ions are withdrawn from the solution. The mercuric-ion concentration remains very low until just after the equivalence-point is reached; even then it is smaller than corresponds to the excess added, since some of the ions are held as a complex:

$$HgCl_2 + Hg^{++} \rightleftarrows 2HgCl^+$$

Mercurimetric methods for determining chloride were proposed long ago. Liebig[1] recommended urea as an indicator, but Mohr[2] preferred to use potassium ferricyanide. The method first achieved practical importance with the introduction, by Votoček,[3] of sodium nitroprusside as indicator. Highly dissociated mercuric compounds give a white precipitate with nitroprusside, while mercuric halides do not. Addition of 0.08 ml. of 0.1 N mercuric nitrate to 100 ml. of water containing 1 ml. of nitric acid and 0.1 g. of sodium nitroprusside produces a permanent turbidity. The quantity of mercuric nitrate required for such a blank should not be considered as a constant correction as has been implied by Votoček. In the presence of mercuric halide some mercuric ions are bound (see above) so that more reagent is required to produce the turbidity. Kolthoff and Bak[4] found that the procedure gives excellent results if the appropriate corrections are determined and subtracted. A particular advantage of the method is that it may be applied to quite strongly acid solutions.

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[1] J. Liebig, *Ann.*, **85**, 297 (1853).

[2] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethoden.* 1st ed., Vol. II, Braunschweig 1860, p. 65.

[3] E. Votoček, *Chem.-Ztg.*, **42**, 257, 271, 317 (1918).

Indicator: Dissolve 10 g. of sodium nitroprusside, $Na_2Fe(CN)_5NO \cdot 2H_2O$, in 90 ml. of water and keep in a brown bottle. Discard if a green color develops.

Standard Mercuric Nitrate Solution (0.1 N): See p. 328 for the direct preparation from pure mercury. Alternatively one may dissolve 16.3 g. of mercuric nitrate in 50 ml. of 1:1 nitric acid, subsequently diluting with water to a liter. This solution should be standardized against pure sodium chloride as in the procedure.

Procedure: To a known volume of halide solution, acidified with nitric acid, add indicator in the ratio of 0.1 ml. to 10 ml. of solution. Filter if it is at all turbid. While observing the mixture against a black background and swirling moderately, titrate slowly with 0.1 N or more dilute mercuric nitrate until a faint but permanent turbidity appears. Subtract a correction (see Tables) for the excess of mercuric reagent that is required.

Corrections: The values listed below were determined by Kolthoff and Bak[4] at 15°C. Their water blank agrees in magnitude with the solubility of mercuric nitroprusside, given by Tomiček and Pročke[5] as somewhat less than 5×10^{-5} M.

MERCURIMETRIC TITRATION OF CHLORIDE AT 15°C.

Final Volume and Concentration of Mercuric Chloride	Correction, ml. 0.1 N Hg^{++}
50 ml. 0.05 N to 100 ml. 0.025 N	0.15–0.20
100 ml. 0.025 N to 100 ml. 0.005 N	0.20–0.15
100 ml. 0.005 N to 100 ml. 0.001 N	0.15–0.12
100 ml. 0.001 N to 100 ml. 0.00025 N	0.12–0.09
100 ml. water	0.07

The junior author has determined corrections which are applicable when one titrates at approximately 25°C. In each case the chloride solution is presumed to be from 0.05 to 0.5 N with respect to nitric acid. A larger proportion of indicator is allowed when 0.02 N mercuric nitrate is employed, to diminish the corrections.

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[4] I. M. Kolthoff and A. Bak, *Chem. Weekblad*, **19**, 14 (1922).

[5] O. Tomiček and O. Pročke, *Collection Czechoslov. Chem. Commun.*, **3**, 116 (1931).

MERCURIMETRIC TITRATION OF CHLORIDE AT 25°C.

100 ml. sample, 1.0 ml. indicator, titrated with 0.10 N $Hg(NO_3)_2$		25 ml. sample, 0.5 ml. indicator, titrated with 0.020 N $Hg(NO_3)_2$	
Observed titration, *ml.*	Correction, *ml.*	Observed titration, *ml.*	Correction, *ml.*
0.08	0.08	0.16	0.16
0.60	0.10	1.20	0.20
1.00	0.12	2.20	0.23
5.00	0.15	3.30	0.26
15.00	0.18	5.30	0.30
25.00	0.20	10.40	0.37

Although the values of the corrections are influenced mainly by the total volumes and concentrations of the halide solutions, it should be emphasized that they are dependent also upon the acidity, and especially upon the rate of titration and manner of viewing the mixture. Evans[6] has succeeded in greatly reducing their magnitude by titrating very slowly and by viewing obliquely against a sloping black background, with illumination from the rear. Under conditions similar to those used in nephelometry (side illumination in a darkened box), Noponen[7] has found that the corrections are further decreased and become almost independent of the amount of halide present. From these facts, it is obvious that for best results an analyst should himself determine correction values appropriate to his own conditions. These can be found by working with solutions prepared from primary standards or by titrating "blanks" to which known amounts of pure mercuric halide have been added.

Notes: (1) Chlorides may be titrated accurately in very dilute solutions; even if only 10 mg. per liter are present the error need not exceed about 2%. The end-point is sharper than that of Mohr's argentometric method. The method is suitable for determining chlorides in potable and industrial waters, various salts, and physiological fluids. Another purpose for which it is useful is in the determination of chloride in bromides, after elimination of the latter with iodate and nitric acid as described on p. 263.

(2) Bromide, thiocyanate, and cyanide (separately) may be titrated in the same way as chloride. When moderately large quantities are present, a correction of 0.13 ml. of 0.1 N solution may be subtracted in the case of bromide or thiocyanate titration, or 0.07 ml. for cyanide. For more exact work, especially with small amounts, the corrections should be found experimentally.

The method is less satisfactory for determination of the total halogen content of a mixture. The corrections vary with different ratios of the constituents.

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[6] L. Evans, unpublished experiments.

[7] G. E. Noponen, private communication.

(3) According to Votoček[8] sulfite interferes but may be eliminated from chloride solutions by careful oxidation with permanganate, followed by the reduction of manganese dioxide with oxalic acid.

(4) Salts of copper, nickel, and cobalt interfere by forming insoluble nitroprussides. No difficulty is encountered with dilute solutions of zinc, ferric iron, bismuth, manganese, aluminum, calcium, strontium, barium, magnesium, or the alkalies. Cadmium behaves in a singular manner: it does not react directly with the indicator but during titration it immediately gives a precipitate that contains also mercury and nitroprusside.

(5) Although the method can be applied to the determination of mercury,[3,9] it is inferior to the thiocyanate procedure (p. 336) for this purpose.

(6) Votoček and Kotrba[10] have proposed an indirect method for cyanide in which it is treated first with an excess of standard mercuric nitrate, then with nitric acid, and finally with an excess of standard sodium chloride, which is titrated mercurimetrically. If chloride is originally present the sum of cyanide and chloride is determined in this way; cyanide alone is found by the method of Denigès (p. 282). One may also titrate the chloride alone by adding formaldehyde, with which hydrocyanic acid forms glycolonitrile.

(b) Diphenyl Carbazide or Diphenyl Carbazone as Indicator: It is well known that diphenyl carbazide and diphenyl carbazone react with mercuric ions giving compounds that are characterized by an intense violet color. Dubský and Trtílek[11] made use of this fact in mercurimetric titrations of chloride. Roberts[12] found that good results are possible only if a p_H between 1.5 and 2.0 is maintained in the solution being titrated. The above indicators are weak acids and behave as acid-base indicators; probably only their alkaline forms give the violet color with mercury. The end-point appears too soon when insufficient acid is present, too late when the acidity is higher.

Reagents: To prepare 0.1 N or 0.025 N mercuric nitrate solution weigh out the proper amount of pure mercuric oxide, suspend in a little water, and add the calculated equivalent quantity of nitric acid. Stir well, add concentrated nitric acid drop by drop until solution is complete, and dilute to volume. The excess acidity should not exceed 0.01 N after dilution.

Solutions of mercuric oxide in perchloric acid may also be employed.

Indicator: Either a saturated solution of diphenyl carbazide in 95% ethanol or a 2% solution of diphenylcarbazone in the same solvent.

Procedures for Chloride, according to Roberts[12]: If one intends to titrate with 0.1 N mercuric nitrate, the sample solution should be adjusted so that it will have a volume of from 80 to 100 ml. at the end-point. Free acid should be neutralized with sodium hydroxide, to an orange color with diphenyl carbazide indicator (5 drops). Then 4 ml. of 0.2 N nitric acid is added and the solution is titrated with mercuric nitrate until the color changes first to a pink-violet and finally to a deep blue-violet. Deduct a blank carried out with the same quantities of acid, water, and indicator.

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[8] E. Votoček, *Z. anal. Chem.*, **125,** 44 (1942).

[9] E. Votoček and L. Kašpárek, *Bull. soc. chim.*, **33,** 110 (1923).

[10] E. Votoček and J. Kotrba, *Collection Czechoslov. Chem. Commun.*, **1,** 165 (1929).

[11] J. V. Dubský and J. Trtílek, *Mikrochemie*, **12,** 315 (1933). *Cf.* K. H. Slotta and J. Müller, *Chem. Fabrik*, **7,** 382 (1934).

[12] I. Roberts *Ind. Eng. Chem., Anal. Ed.*, **8,** 365 (1936).

To titrate with 0.025 N mercuric nitrate, adjust so that the final volume will be from 55 to 75 ml. Add 2 drops of 0.2% bromophenol blue and neutralize any acidity or alkalinity so that the solution is just at a full blue color. Introduce 4 ml. of 0.2 N nitric acid and 5 drops of diphenyl carbazide indicator. While observing the solution under a daylight lamp, titrate to a definite pink with mercuric nitrate. Determine the blank as before, but in the presence of a quantity of acid equal to that contained in the mercuric nitrate solution used for the sample.

Notes: (1) Cadmium, cobalt, ferrous iron, lead, and copper give orange or red to violet colors or precipitates with the indicator, but interference is prevented by the addition of 0.2 N nitric acid as specified.

(2) The procedure can be employed for determination of mercuric salts by adding an excess of standard chloride solution and back-titrating. Dubský and Trtílek[13] have applied a similar method to the determination of silver, particularly in the presence of copper.

Determination of Bromide: According to Trtílek,[14] the mercurimetric method is also useful for bromide titration if at the end-point the solution is 0.15 to 0.2 N in nitric acid. As indicator, 0.1 to 0.2 ml. of cold saturated diphenyl carbazone in alcohol is used. Results accurate to within 1% are reported. With small amounts of bromide significant errors are caused by variations in the final acidity.

Procedures for thiocyanate and cyanide have also been developed,[15] but do not appear to offer any advantage over other methods for these ions.

Determination of Iodide: Very dilute iodide solutions may be titrated mercurimetrically with diphenyl carbazide as indicator.[16] However, if the concentration of iodide is greater than about 0.0003 N, red mercuric iodide precipitates and interferes. Jilek and Koudela[17] found that the addition of pyridine to a dilute nitric acid solution of the sample prevents this by forming with mercuric iodide a white insoluble complex which remains in colloidal suspension during the titration. To 50–100 ml. of neutral solution containing at most 130 mg. of iodine, as iodide, one adds 2 ml. of

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[13] J. V. Dubský and J. Trtílek, *Z. anal. Chem.*, **93**, 345 (1933).

[14] J. Trtílek, *Collection Czechoslov. Chem. Commun.*, **10**, 97 (1938). Also H. R. McCleary, *Ind. Eng. Chem., Anal. Ed.*, **14**, 31 (1942).

[15] J. Trtílek, *Collection Czechoslov. Chem. Commun.*, **10**, 242 (1938).

[16] J. V. Dubský and J. Trtílek, *Mikrochemie*, **15**, 95 (1934).

[17] A. Jilek and G. Koudela, *Collection Czechoslov. Chem. Commun.*, **9**, 265 (1937).

0.5 N nitric acid and 5.7 ml. of a 1:9 solution of pyridine in water. The mixture is titrated with 0.02 N mercuric nitrate, using diphenyl carbazide as indicator, until the color changes to blue.

Notes: (1) Cadmium interferes somewhat by giving a weak color with the indicator, but ferrous sulfate and the alkaline earth ions are harmless. In the presence of chloride the ratio of pyridine to nitric acid must be varied, depending upon the ratio of chloride to iodide.

(2) To determine thallous thallium, Trtílek[18] precipitates it with an excess of standard iodide solution in the presence of ammonium nitrate. The neutral or very weakly acid suspension is made to volume and filtered without washing; an aliquot part of the filtrate is titrated mercurimetrically as has been described.

McCleary[19] obtained good results in the titration of iodide by adding enough dioxane to make its concentration 10 to 15% by volume. Under these conditions mercuric iodide precipitates in a metastable yellow form which does not interfere with the indicator change. The dioxane must be free from peroxides; it may be purified by distillation from sodium and stabilized for up to two weeks by addition of 0.5 g. of hydroquinone per liter.

Procedure: Take a sample containing 15 to 60 mg. of iodine and neutralize, if necessary, to phenolphthalein. Allowing for the acidity of the mercuric nitrate solution (p. 334) add enough 0.2 N nitric acid so that 5 ml. of 0.2 N acid will be present at the end-point. Dilute with water to make the total final volume between 55 and 75 ml. Introduce 8 ml. of peroxide-free dioxane and titrate quickly with 0.025 N mercuric nitrate solution to within 2 or 3 ml. of the expected end-point. (The titer is roughly twice the volume of reagent added before yellow mercuric iodide begins to precipitate.) Add 15 drops of saturated diphenyl carbazide in alcohol and continue titrating to a sharp change from yellow to blue-gray. Subtract an indicator correction of 0.07 ml.

Note: After 5 or 10 minutes the red form of mercuric iodide appears. The titration must be completed prior to this change.

2. Determination of Mercury with Thiocyanate.—Although mercuric thiocyanate is only very slightly dissociated, the thiocyanate-ion concentration of a saturated solution containing a little nitric acid is sufficient to give a faint color with ferric alum. The red-brown shade becomes more distinct at temperatures above 20°C. If one titrates a mercuric solution with thiocyanate, using ferric alum as the indicator, the end-point appears somewhat too soon. Volhard[20] long ago described the determination of mercury with thiocyanate and recognized the premature end-point.

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[18] J. Trtílek, *Z. anal. Chem.*, **111**, 10 (1937).

[19] H. R. McCleary, *Ind. Eng. Chem., Anal. Ed.*, **14**, 31 (1942).

[20] J. Volhard, *Ann.*, **190**, 57 (1878).

It is advantageous to have the nitric acid concentration small, although Rupp[21] found, and it was confirmed by the senior author, that at low temperatures the acid concentration scarcely influences the result. With increasing temperature the effect of excessive acidity becomes greater. It is best for very precise work to titrate at 15°C. The end-point may then be recognized quite exactly although the accuracy generally is not better than to 0.3%.

Procedure: Prepare the sample so that from 0.1 to 0.3 g. of mercuric mercury is present in 100 ml. of solution containing about 10 ml. of 6 N nitric acid. (Mercurous compounds may be oxidized by dropwise addition of 5% potassium permanganate solution until the permanganate color persists. The excess oxidant or manganese dioxide should be reduced with a very small excess of ferrous sulfate solution.) Cool the solution to below 15°C., add 1 ml. of saturated ferric alum indicator and titrate with 0.1 N thiocyanate, slowly and with good agitation, to a permanent reddish brown color. Standardize the thiocyanate solution in the same way, against a standard mercuric solution (see Note 6 below) or a weighed quantity of mercuric oxide.

If the titration is carried out at room temperature, one should employ a reference solution saturated with mercuric thiocyanate and containing the proper quantities of indicator and acid.

Notes: (1) Mercuric thiocyanate is not very soluble in water, but it remains dissolved during the titration because of complex formation with mercuric ions. It also has a tendency to form supersaturated solutions, according to Karaoglanov.[22] Precipitation is likely to take place near the equivalence-point.

(2) Derivation of the titration error is difficult since the final concentration of mercuric thiocyanate is variable and also since this substance enters into complexes with either of its constituent ions:

$$Hg(CNS)_2 + Hg^{++} \rightleftarrows 2Hg(CNS)^+$$

$$Hg(CNS)_2 + (1 \text{ or } 2)CNS^- \rightleftarrows Hg(CNS)_3^- \text{ or } Hg(CNS)_4^{=}$$

For these reasons the course of the ion concentrations near the equivalence-point can hardly be calculated. Practically, however, the titration error is negligible at temperatures below 15°C.

From what has been said it follows that the color change is not sharp. The thiocyanate-ion concentration does not increase greatly at the end-point.

(3) Kolthoff and Lingane[23] have shown that small deviations from the theo-

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[21] E. Rupp, *Arch. Pharm.*, **241**, 444 (1903); *Chem.-Ztg.*, **32**, 1077 (1908). E. Rupp and L. Krauss, *Ber.*, **35**, 2015 (1902).

[22] Z. Karaoglanov, *Z. anal. Chem.*, **125**, 406 (1943).

[23] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, **57**, 2377 (1935).

retical titers can be ascribed to side reactions occurring when mercury is titrated with thiocyanate, or vice versa. A trace of ammonia is formed by the decomposition of thiocyanate. However, the errors resulting from this cause are negligible, of the order of 0.05%.

(4) Chloride interferes in the mercury determination because mercuric chloride is also slightly dissociated and therefore does not become completely converted to thiocyanate. Bromide interferes even more strongly, since the dissociation constants of mercuric bromide and mercuric thiocyanate have the same order of magnitude. However, the interference is not quantitative and attempts to determine bromide by means of mercuric nitrate titration with ferric thiocyanate as indicator have been unsuccessful. The end-point comes much too soon. No improvement results from adding an excess of mercuric solution and back-titrating with thiocyanate.

Phosphate also interferes in the determination of mercury.[22] A general method for separating mercury from halides or phosphate consists in precipitating it as the sulfide and filtering on a 7 cm. paper. The washed precipitate and paper are transferred to a Kjeldahl flask and treated with 6 ml. of concentrated sulfuric acid. Several glass beads are introduced, followed by 10 ml. of hydrogen peroxide.[24] After the reaction has subsided the flask is warmed with a small flame and finally heated to fumes of sulfuric acid. Any remaining brown color should be cleared by cautious additions of peroxide and further heating. The mixture is then cooled and diluted in preparation for thiocyanate titration.

Silver may be removed by precipitation with an excess of hydrochloric acid, prior to the sulfide separation. Sufficient chloride must be present to transform all mercury to $HgCl_4^=$, before silver precipitates.

(5) The procedure for mercury may be reversed to provide a determination of thiocyanate, the titration being carried to disappearance of the color. Because of complex formation, fading begins long before the equivalence-point. Nevertheless the final change may be recognized quite distinctly; in fact, Cohn[25] preferred to titrate in this direction when determining mercury, by adding an excess of thiocyanate and titrating back with standard mercuric solution. The authors do not feel that this indirect approach is necessary.

(6) Mercury is an excellent primary standard substance for standardizing thiocyanate. Ordinary mercury may be purified by filtration, washing with 5% nitric acid or a mercurous nitrate solution[26] and distillation in vacuum. The surface should be entirely clean and the residue left after volatilization of 10 g. should not exceed 1 mg.

To prepare a 0.1 N solution, dissolve 10.030 g. of mercury by warming with 50 ml. of 50% nitric acid in a Kjeldahl flask. Boil out the lower oxides of nitrogen, cool, and dilute to one liter in a volumetric flask.

Standardization is performed as indicated in the procedure on p. 337. At a temperature below 15°C. the standardization is quite exact without a reference solution. Kolthoff and van Berk[27] found the effective strengths of pure mercury and pure silver to be identical (100.0%). In contrast, some C.P. preparations of mercuric oxide showed effective strengths of only 99.8%.

(7) Organic matter in organic mercurial compounds is destroyed by refluxing with sulfuric acid and potassium sulfate, according to Rupp and Nöll,[28] after which the mercury may be determined as has been described. Schulek and Floderer[24] use sulfuric acid and hydrogen peroxide; they studied methods for mercury in various pharmaceuticals.

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[24] E. Schulek and S. Floderer, *Z. anal. Chem.*, **96**, 388 (1934).

[25] R. Cohn, *Ber.*, **34**, 3502 (1901).

[26] H. F. Easly, *Ind. Eng. Chem., Anal. Ed.*, **9**, 82 (1937). J. H. Hildebrand, *J. Am. Chem. Soc.*, **31**, 933 (1909).

[27] I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, **71**, 339 (1927).

[28] E. Rupp and P. Nöll, *Arch. Pharm.*, **243**, 1 (1905).

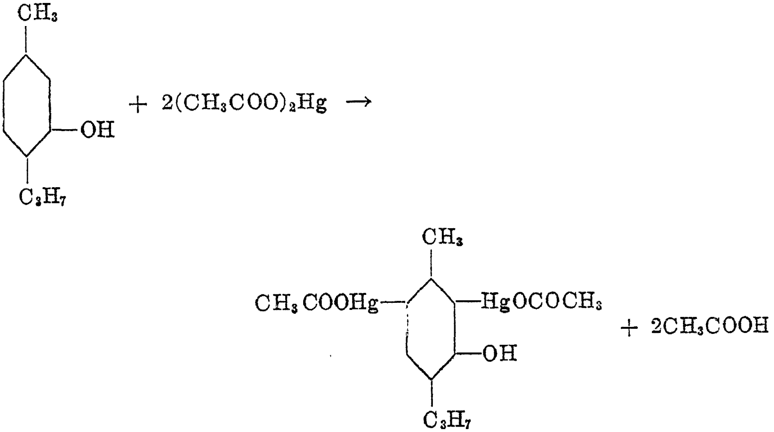
Stschigol[29] removes mercury from organic or inorganic compounds by reducing it with glycerine in alkaline solution:

$$HgO + CH_2OHCHOHCH_2OH \rightarrow Hg + H_2O + CH_2OHCHOHCHO$$

The metallic mercury is filtered out, washed, dissolved in nitric acid, and titrated with thiocyanate. The reduction of mercury compounds with ethanolamine, with or without sodium and dioxane, has been described by Rauscher.[30] This furnishes a convenient method of separating mercury from halogens.

Determination of Cyanide: Mercuric cyanide is much less dissociated than mercuric thiocyanate. Therefore if to a cyanide solution there are added an excess of standard mercuric nitrate and some nitric acid, the excess mercury may be titrated back with thiocyanate. The procedure is somewhat more convenient than that of Volhard (p. 281). To determine free hydrocyanic acid in bitter almond water one treats 50 ml. of the water with 10 ml. of 0.1 N or 0.05 N mercuric nitrate, 5 ml. of 4 N nitric acid, and 0.5 ml. of saturated ferric alum indicator, then titrates with thiocyanate. Each milliliter of 0.1 N mercuric solution consumed corresponds to 2.70 mg. of hydrogen cyanide.

Determination of Thymol: It was found by Rupp[31] that thymol reacts with mercuric acetate to form a dimercuric substitution product:



Bordeianu[32] made use of the reaction for assaying thymol; the unused portion of the mercuric acetate is titrated with thiocyanate.

Procedure: Weigh accurately about 0.5 g. of mercuric oxide in a 25 ml. Erlenmeyer flask and dissolve it completely in 1.5 ml. of acetic acid. Add

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[29] M. Stschigol, *Z. anal. Chem.*, **96**, 330 (1934).

[30] W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 331 (1938). F. A. Rotondaro, *J. Am. Pharm. Assoc.*, **33**, 353 (1944).

[31] E. Rupp, *Arch. Pharm.*, **255**, 191 (1917).

[32] C. V. Bordeianu, *Z. anal. Chem.*, **91**, 421 (1933).

0.1 g. of the thymol, also weighed accurately, and stir until it is dissolved. Introduce 1 ml. of water, stopper the flask with a cork through which a long, thin glass tube passes, and warm for half an hour on a steam bath. Allow to cool, dilute with water, let stand for 5–10 minutes and filter. Wash the precipitate with a warm 1% solution of acetic acid in water. Acidify the combined filtrate and washings with nitric acid and titrate the mercury with thiocyanate in the presence of ferric alum. At the end-point the mixture is light yellow to yellow-brown. An error of about 0.6% is likely in the thymol determination.

Determination of Zinc as Zinc Mercuric Thiocyanate: With an excess of alkali thiocyanate, mercuric thiocyanate forms a complex that is capable of precipitating zinc and several other metals:

$$Hg(CNS)_2 + 2CNS^- \rightleftarrows Hg(CNS)_4^=$$
$$Hg(CNS)_4^= + Zn^{++} \rightleftarrows ZnHg(CNS)_4$$

Cohn[33] applied the reaction to zinc determinations, but his original procedure failed to give reliable values. De Koninck and Grandry[34] introduced potassium mercuric thiocyanate as a volumetric reagent and obtained satisfactory results. A solution which is quite stable can be prepared as described below.[35]

Reagent: Dissolve 14.4 g. of potassium thiocyanate in a little water, add 23.7 g. of mercuric thiocyanate, and shake, eventually warming gently, until all the crystals are dissolved. Dilute to one liter with water; 25 ml. of the solution will consume about 37.5 ml. of 0.1 N mercuric nitrate when titrated with ferric alum as indicator. A solution prepared from mercuric nitrate, potassium thiocyanate, and nitric acid is not stable since thiocyanate is decomposed by the acid.

Procedure: To 25 ml. of an approximately 0.1 N zinc solution, which may also contain free sulfuric or nitric acid, add 25 ml. of reagent, accurately measured. Dilute the mixture to 100 ml. in a volumetric flask, shake thoroughly, and filter without washing. Pipette out 50 ml. of the filtrate, add ferric alum indicator, and titrate with standard mercuric nitrate. Dilute another 25 ml. portion of the reagent in the same way, without addition of zinc, and titrate 50 ml. of the filtrate. The difference between the titrations represents half the quantity of thiocyanate combined with zinc. Results are accurate to within 0.5%.

Notes: (1) Precipitation takes place quickly if the zinc concentration is greater than 0.01 N. More dilute solutions should be allowed to stand 24 hours before filtration. Under such conditions no free mineral acid should be present since it would destroy part of the thiocyanate and high results would be obtained. The analysis of such a dilute solution is not entirely satisfactory even if it is neutral, however, for the uncertainty of end-point recognition amounts to 0.2 or 0.3 ml. of 0.01 N solution. There is also an error caused by the solubility of zinc mercuric thiocyanate. The solubility amounts to 7.4×10^{-4} N in water, 1.2×10^{-4} N in 0.0015 N potassium mercuric thiocyanate, 3×10^{-5} in 0.003 N reagent, and 1×10^{-5} N in 0.006 N reagent. It is best to work with zinc solutions that are stronger than 0.02 N and to have sufficient excess reagent to make its concentration at least 0.006 N.

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[33] R. Cohn, *Ber.*, **34,** 3502 (1901).

[34] L. L. de Koninck and M. Grandry, *Chem. Zentr.*, **73, II,** 822 (1902).

[35] I. M. Kolthoff and J. C. van Dyk, *Pharm. Weekblad*, **58,** 549 (1921). According to E. Monasch, *ibid.*, **58,** 1652 (1921), the reagent does not change within at least 4 months.

(2) Halides and other substances which react with mercuric ions would naturally interfere.

(3) The investigations of Monasch[35] showed that aluminum and ferric iron are not objectionable. On the other hand, copper, nickel, manganous, ferrous, and chromic ions were found to cause definite interference. A smaller interference was noted with bismuth. Cobalt was not tested but would presumably be as harmful as nickel.

Copper may be removed by precipitation on metallic aluminum, after which the solution may be titrated as has been described.

(4) Titus and Olsen[36] do not titrate the excess of reagent, but wash the precipitate with 50–75 ml. of 0.001 M reagent at 0°C. and then dissolve it in an excess of standard iodide solution. The latter is titrated with 0.1 N mercuric nitrate until a permanent trace of red mercuric iodide appears. As is mentioned on p. 342, the end-point does not coincide with the equivalence-point; nevertheless, fairly good results can be secured with the use of a determined correction. Chief advantage of the method is that chloride and some other interfering ions are eliminated in the filtrate. Possibly the same end might be attained more directly by titrating the precipitate (in a strongly acid solution, see p. 337) with mercuric nitrate until all of the thiocyanate is bound as $Hg(CNS)_2$.

Other Elements: Spacu and his collaborators advocate the determination of various metal ions by precipitation of double thiocyanates with pyridine and alkali thiocyanate.[37] Copper, zinc, nickel, cobalt, and even pyridine can be determined in this way, but the methods are not described here because of their lack of specificity.

Determinations of copper involving precipitation of cuprous thiocyanate[33] or cupric mercuric thiocyanate[38] have been proposed but are of little practical use (see, however, p. 329).

3. Determination of Iodide with Mercuric Chloride.—If a mercuric salt is gradually added to an iodide solution, there is first formed the complex mercuric iodide ion $HgI_4^{=}$. Near the equivalence-point mercuric iodide begins to precipitate:

$$HgI_4^{=} + Hg^{++} \rightleftarrows 2HgI_2$$

As long ago as 1832 the reaction was applied by Marozeau[39] to the assay of potassium iodide; it was proposed independently by Probst[40] for the determination of mercuric chloride. Other workers[41] described the method anew, for either purpose. In order to determine mercuric chloride, one adds an excess of standard potassium iodide and titrates back with mercuric chloride solution. The titration error has been discussed in Volume I, pp. 154–6. Duflos[42] recognized a century ago that the red turbidity appears too soon, and this was confirmed by others.[43] Auerbach and Plüddemann,[44] as well as Kolthoff,[45] have studied the method and derived corrections for the premature end-point. An appropriate value from the following table should be added to the observed titration volume.

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[36] A. C. Titus and J. S. Olsen, *Ind. Eng. Chem., Anal. Ed.*, **12**, 133 (1940).

[37] See, for example, G. Spacu and M. Kuras, *Z. anal. Chem.*, **99**, 26 (1934).

[38] J. Volhard, *Ann.*, **190**, 51 (1878). R. Henriques, *Chem.-Ztg.*, **16**, 1597 (1892). H. Theodor, *ibid.*, **32**, 889 (1908). O. Kuhn, *ibid.*, **32**, 1056 (1908). G. Fernekes and A. A. Koch, *J. Am. Chem. Soc.*, **27**, 1224 (1905).

[39] Marozeau, *J. pharm. chim.*, **18**, 302 (1832) (J. Berzelius, *Jahresber.*, **1834**, p. 126).

CORRECTIONS FOR TITRATION OF IODIDE WITH MERCURIC CHLORIDE

Final Volume, *ml.*	Correction, ml. 0.05 M $HgCl_2$
37	0.60
50	0.73
75	0.91
100	1.05
125	1.14

Procedure: Dissolve the iodide in a volume of water as small as is conveniently possible. Titrate with 0.05 M mercuric chloride solution, meanwhile stirring or swirling thoroughly, until a red turbidity appears and remains permanently. Estimate the final volume of the mixture and apply a correction as indicated above.

The yellow form of mercuric iodide appears first, but quickly changes to the more stable red modification.

Notes: (1) Variations of temperature are insignificant if one works between 10° and 30°C.[45,46]

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[40] Probst (1840), quoted in H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig 1913, p. 999. Other early literature on this subject is also quoted from Beckurts.

[41] J. Personne, *Compt. rend.*, **56**, 951 (1863). Portes and Ruyssen, *ibid.*, **82**, 1504 (1876). O. Kaspar, *Schweiz. Wochschr. Pharm.*, **1881**, 189. Herbelin, *J. pharm. chim.*, **8**, 125 (1883). Sasse, *Pharm. Ztg.*, **1887**, 740. C. Montanari, *Gazz. chim. ital.*, **33**, **I**, 155 (1903).

[42] A. Duflos, *Chem. Apothekerbuch*, **1843**, p. 513; **1845**, p. 485.

[43] J. Otto, *Lehrbuch der Chemie*, 3rd ed., Vol. II, 1853, p. 110. F. Mohr, *Titriermethode*, Vol. II, 1860, p. 81.

[44] F. Auerbach and W. Plüddemann, *Arb. kaiserl. Gesundh.*, **1**, 209 (1909); *Chem. Zentr.*, **1909**, **I**, 688.

[45] I. M. Kolthoff, *Pharm. Weekblad*, **57**, 836 (1920).

[46] Meyer, *Pharm. J.* (*Russia*), **24**, 514 (1895).

(2) The red turbidity appears too late in the presence of much hydrochloric acid or of a little bromide or thiocyanate, since these substances bind mercuric ions. On the other hand, sulfuric acid, alcohol, and sugar have no unfavorable effect and the procedure is therefore suitable for the analysis of iron iodide syrups.

(3) Under somewhat different conditions Titus and Olsen[47] found a larger value for the correction than would be expected from the foregoing.

Determination of Formic Acid: As was mentioned previously, the preceding method may be adapted for mercuric chloride assay by adding standard iodide and titrating the excess. Portes and Ruyssen[41] have made application of this fact in the determination of formic acid. Below is given their procedure as modified by Auerbach and Plüddemann.[44] Formic acid reduces mercuric chloride to slightly soluble calomel:

$$HCOOH + 2HgCl_2 \rightarrow 2HgCl + CO_2 + 2HCl$$

and the excess of mercuric salt is determined by titration.

Reagents: Dissolve 58.87 g. of mercuric chloride and 12 g. of sodium chloride in water and dilute to one liter. 1 ml. corresponds to 5.0 mg. of formic acid.

Prepare a 1.25 N solution of very pure potassium iodide and keep it in the dark.

Procedure: Take an amount of sample containing 20–70 mg. (preferably 30–50 mg.) of formic acid, neutralize, and if necessary evaporate to a small volume. Place in a 100 ml. volumetric flask and add 3 g. of formate-free sodium acetate and a slight excess of mercuric chloride solution over the expected requirement. Measure this reagent accurately. Bring the mixture to a volume of somewhat less than 100 ml., immerse the flask up to its neck in boiling water for two hours, then cool and fill to the mark. Mix the contents, filter through a dry, folded filter, and catch in a dry flask, discarding the first portion of filtrate. Place the filtrate in a burette and with it titrate exactly 2 ml. of 1.25 N potassium iodide, to the first appearance of a reddish color.

CORRECTION FACTORS FOR FORMIC ACID DETERMINATION

v	f	v	f
20	1.036	50	1.069
25	1.042	55	1.074
30	1.047	60	1.079
35	1.052	65	1.084
40	1.058	70	1.090
45	1.063	75	1.095

If v in the table above represents the observed titration volume, then f is the factor, according to Auerbach and Plüddemann, by which v should be multiplied to obtain the corrected volume (in ml.) of mercuric chloride solution equivalent to 2 ml. of 1.25 N iodide.

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[47] A. C. Titus and J. S. Olsen, *Ind. Eng. Chem., Anal. Ed.*, **12**, 133 (1940).

Note: The method is suitable only for purposes in which high accuracy is unnecessary. Bromometric[48] or gravimetric determination of the precipitated calomel would probably be more satisfactory.

4. Miscellaneous Methods.—*Determination of Platinum Metals with Sodium Diethyldithiocarbamate:* It has been found by Pollard[49] that small quantities of platinum and palladium in solution as divalent chlorides can be titrated with an aqueous solution of sodium diethyldithiocarbamate. Since both elements react with this reagent they must be separated first, for which purpose precipitation of the palladium with α-nitroso-β-naphthol is recommended. Platinous chloride is colored and upon titration with diethyldithiocarbamate solution it is decolorized. In the case of palladium the original color is transient but is intensified by a trace of mercuric chloride and the latter does not interfere with the titration.

Reagents: Dissolve 0.5 g. of sodium diethyldithiocarbamate in 100 ml. of water and filter off any oily impurities. Standardize freshly against a known quantity of palladium, as in the procedure. Discard when more than a month old.

Palladium solution: Dissolve 0.1 g. of palladium metal in 1.5 ml. of hydrochloric acid and 0.5 ml. of nitric acid. When dissolved, dilute to 100 ml. 1 ml. contains 1 mg. of palladium.

Stannous chloride solution: Heat 500 g. of stannous chloride dihydrate with 200 ml. of strong hydrochloric acid and some granulated tin, for several hours on a water bath. Filter through asbestos and keep well-stoppered.

Procedure for Palladium: Prepare the sample so that from 0.01 to 1.0 mg. of palladium, free from platinum, is present in approximately 10 ml. of 1:1 hydrochloric acid, in a test tube. Add 1 ml. of stannous chloride solution and when the brownish color has developed introduce 5 ml. of benzene. Titrate with diethyldithiocarbamate solution, using a microburette. After each addition close the tube with a rubber stopper, shake, and allow the layers to separate. When the aqueous solution is nearly colorless, add 5 drops of 0.01% mercuric chloride solution and shake until the red-brown color develops. Continue the titration until the aqueous layer is entirely colorless.

For weaker solutions (0.001 to 0.01 mg. palladium) use 2 ml. of 1:1 acid, 2 drops of stannous chloride, and one drop of mercuric chloride. Titrate with a 1:10 dilution of the carbamate.

Note: Sulfates, iodides, and many metals interfere.

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[48] F. Oberhauser and W. Hensinger, *Z. anorg. allgem. Chem.*, **160**, 366 (1927). *Cf.* also Volume III.

[49] W. B. Pollard, *Bull. Inst. Mining Met.*, Nos. **400**, **406**, (1938); *Trans. Inst. Min. Met.*, **47**, 331 (1938); **48**, 65 (1939); *Analyst*, **67**, 184 (1942). *Cf. Chem. Abstracts*, **36**, 5440 (1942); **32**, 1610, 7854 (1938); **33**, 9197 (1939).

APPENDIX

Atomic Weights

Atomic weight tables issued by the Committee on Atomic Weights of the International Union of Chemistry,[1] or by the Committee on Atomic Weights of the American Chemical Society,[2] are based upon weighings which have been corrected for the buoyancy of air. In very exact analytical work it is necessary to apply similar corrections to the weights of samples and standard substances. As Schoorl has pointed out (see p. 35), the need for corrections may be avoided if one makes use of *rational atomic weights* in calculating the amounts of standard substance to be weighed, or of material found, in a volumetric process. Schoorl derived a table of rational values, referred to the use of brass weights in air of ordinary density and based upon the assumption that the atomic volumes of the elements are additive in their compounds. The error introduced by this assumption is relatively small.

In Table I the elements are listed alphabetically according to their symbols, and the international atomic weights for 1941 appear in the third column. Rational atomic weights, taken from Schoorl's table but corrected for changes in the older international weights, appear in the fourth column. The last column gives practical atomic weights rounded to within 0.1%; these are sufficiently accurate for the calculations of most analyses.

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[1] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, *J. Am. Chem. Soc.*, **63**, 845 (1941).

[2] G. P. Baxter, *J. Am. Chem. Soc.*, **65**, 1443 (1943).

(See Table I, pp. 346–7)

TABLE I

Element	Symbol	International Atomic Weight	Rational Atomic Weight	Rounded Value
Silver	Ag	107.88	107.88	107.9
Aluminum	Al	26.97	26.96	27.0
Arsenic	As	74.91	74.90	74.9
Gold	Au	197.2	197.2	197.2
Boron	B	10.82	10.81	10.8
Barium	Ba	137.36	137.36	137.4
Beryllium	Be	9.02		9.02
Bismuth	Bi	209.00	209.01	209.0
Bromine	Br	79.916	79.90	79.9
Carbon	C	12.010	12.01	12.0
Calcium	Ca	40.08	40.07	40.1
Cadmium	Cd	112.41	112.41	112.4
Cerium	Ce	140.13		140.1
Chlorine	Cl	35.457	35.44	35.44
Cobalt	Co	58.94	58.94	58.9
Chromium	Cr	52.01	52.00	52.0
Cesium	Cs	132.91		132.9
Copper	Cu	63.57	63.57	63.6
Europium	Eu	152.00		152.0
Fluorine	F	19.00	19.00	19.0
Iron	Fe	55.85	55.84	55.8
Gallium	Ga	69.72		69.7
Germanium	Ge	72.60		72.6
Hydrogen	H	1.0080	1.001	1.00
Mercury	Hg	200.61	200.61	200.6
Iodine	I	126.92	126.90	126.9
Indium	In	114.76		114.8
Potassium	K	39.096	39.076	39.1
Lanthanum	La	138.92		138.9
Lithium	Li	6.940	6.940	6.94
Magnesium	Mg	24.32	24.32	24.3
Manganese	Mn	54.93	54.93	54.9
Molybdenum	Mo	95.95	95.95	96.0
Nitrogen	N	14.008	14.00	14.0
Sodium	Na	22.997	22.99	23.0
Neodymium	Nd	144.27		144.3
Nickel	Ni	58.69	58.69	58.7
Oxygen	O	16.000	15.995	16.0
Osmium	Os	190.2	190.2	190.2
Phosphorus	P	30.98	30.97	31.0
Lead	Pb	207.21	207.22	207.2
Palladium	Pd	106.7		106.7
Praseodymium	Pr	140.92		140.9
Platinum	Pt	195.23	195.24	195.2

TABLE I—*Concluded*

Element	Symbol	International Atomic Weight	Rational Atomic Weight	Rounded Value
Rubidium	Rb	85.48		85.5
Rhenium	Re	186.31		186.3
Sulfur	S	32.06	32.045	32.05
Antimony	Sb	121.76	121.75	121.8
Selenium	Se	78.96	78.96	79.0
Silicon	Si	28.06	28.05	28.05
Tin	Sn	118.70	118.70	118.7
Strontium	Sr	87.63	87.62	87.6
Tantalum	Ta	180.88		180.9
Tellurium	Te	127.61	127.6	127.6
Thorium	Th	232.12		232.1
Titanium	Ti	47.90	47.9	47.9
Thallium	Tl	204.39	204.39	204.4
Uranium	U	238.07	238.07	238.1
Vanadium	V	50.95	50.95	51.0
Tungsten	W	183.92	183.92	184.0
Yttrium	Y	88.92		88.9
Zinc	Zn	65.38	65.38	65.4
Zirconium	Zr	91.22		91.2

Index to Standard Substances

In Table II are listed the standard substances mentioned in this volume and the numbers of the pages on which they are described. With the description of each there will generally be found its international equivalent weight and the corresponding rational weight, for weighing in air. For convenience, some of the data concerning the more highly recommended compounds are repeated in the table, where the chemical formula, the number of equivalents per mole, the rational equivalent weight, and its logarithm are also given. The rational weights are those of Schoorl, corrected for subsequent changes in the international atomic weight table; they take into account the densities of the substances. Where no rational weight is listed, recommendation has been withheld for reasons mentioned in the text.

(*See Table, p. 348*)

TABLE II

Standard	Page	Formula	Equivalents per Mole	Rational Equivalent Weight	$\log_{10}$
ACIDIMETRY					
Borax		$Na_2B_4O_7 \cdot 10H_2O$	2	190.60	.28012
Calcite	86	$CaCO_3$	2		
Diphenylguanidine	92	$(C_6H_5NH)_2CNH$	1		
Mercuric oxide	90	HgO	2	108.30	.03463
Potassium bicarbonate	84	$KHCO_3$	1	100.07	.00030
Potassium bitartrate		$KHC_4H_4O_6$	1		
Potassium iodate		KIO_3	6	35.66	.55218
Sodium bicarbonate	84	$NaHCO_3$	1		
Sodium carbonate	79	Na_2CO_3	2	52.99	.72419
Sodium chloride	92	$NaCl$	1		
Sodium oxalate	74	$Na_2C_2O_4$	2	66.99	.82601
Sodium thiosulfate	90	$Na_2S_2O_3 \cdot 5H_2O$	1		
Thallous carbonate	83	Tl_2CO_3	2	234.38	.36992
ALKALIMETRY					
Adipic acid	102	$H_2C_6H_8O_4$	2		
Benzoic acid	94	$HC_7H_5O_2$	1	122.07	.08661
Borax	102	$Na_2B_4O_7 \cdot 10H_2O$	2		
Cadmium sulfate	103	$CdSO_4 \cdot 8/3H_2O$	2		
Furoic acid	102	$HC_5H_3O_3$	1		
Hydrazine sulfate	102	$N_2H_4 \cdot H_2SO_4$	2	65.02	.81305
Oxalic acid	94	$H_2C_2O_4 \cdot 2H_2O$	2	63.00	.79934
Potassium bi-iodate	100	KHI_2O_6	1	389.85	.59090
Potassium bioxalate	101	KHC_2O_4	1		
Potassium biphthalate	94	$KHC_8H_4O_2$	1	204.14	.30993
Potassium tetroxalate	101	$KH_3C_4O_8 \cdot 2H_2O$	3		
Pseudocumene sulfonic acid	102	$HC_9H_{11}O_3S \cdot 2H_2O$	1		
Salicylic acid	102	$HC_7H_5O_3$	1		
Sulfamic acid	99	HSO_3NH_2	1		
Other substances	103				
PRECIPITATION AND COMPLEX FORMATION METHODS					
Mercuric oxide	90	HgO	2	108.30	.03463
Mercury	338	Hg	2	100.30	.00130
Potassium bromide	252	KBr	1	118.98	.07548
Potassium chloride	252	KCl	1	74.52	.87227
Potassium ferrocyanide	302	$K_4Fe(CN)_6$			
Potassium thiocyanate	252	$KCNS$	1	97.13	.98735
Silver	254	Ag	1	107.88	.03294
Silver nitrate	253	$AgNO_3$	1	169.87	.23011
Sodium chloride	251	$NaCl$	1	58.43	

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